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ON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE AND THE MECHANISM OF INDUCED OXIDATIONS. TOGETHER WITH A NOTE ON THE NATURE AND FUNCTION OF CATALASE.

PART I.

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THE ACTION OF INHIBITORS ON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE.

The decomposition of hydrogen peroxide by various substances, under different conditions, has been the subject of a large number of investigations. The theories of oxidation which have been advanced from time to time have largely centered around studies upon this peroxide and its catalytic decomposition, and hence the most important views which have been held may be here mentioned. Even in his earlier work upon hydrogen peroxide, Thénard[1] reached the conclusion that all substances exert some effect on this substance, some, like the acids, tending to increase its stability, others, like the metallic oxides and the finely divided metals, tending to decompose it. Schönbein made a very careful study of the

[1] Ann. chim. phys., 9, 314 (1818).

catalytic decomposition of hydrogen peroxide and induced oxidations, the results of which he presented in a series of very interesting papers.[1] He pointed out that animal and vegetable extracts from the most diverse sources possess the power of decomposing hydrogen peroxide, and he looked upon this reaction as the prototype of fermentative activity.

Following the work of Schönbein, it was generally believed that all ferments, besides being able to effect their specific reactions, also possessed, in common, the power to decompose hydrogen peroxide. The work of Jacobson,[2] however, indicated that this is not the case. He showed that solutions of enzymes may be made to lose their power of decomposing hydrogen peroxide without losing their specific properties. Spitzer[3] studied the organs of the body with reference to their relative power to decompose hydrogen peroxide, and found them to stand in about the same order as was found by Abelous and Biarnés,[4] and by Salkowski,[5] who measured the oxidation of salicylic aldehyde by these tissues.

From this correlation existing between the power of tissues to decompose hydrogen peroxide and their power to oxidize salicylic aldehyde, Spitzer was led to believe that the two processes have the same cause, and that the power to decompose hydrogen peroxide is, therefore, a true index of the oxidizing power of the tissues. Recently two pieces of work on this catalytic decomposition have attracted much attention. Loew[6] has shown that the decomposition of hydrogen peroxide by plant extracts is not brought about by enzymes in general, but by a specific enzyme of universal occurrence in living organisms, to which he has given the name catalase. Bredig[7] and his pupils have carefully studied the decomposition of hydrogen peroxide by "pseudo solutions" of the colloidal metals. Quite recently Kastle and Clark[1] have shown that many substances, such as copper sulphate, chrome alum, etc., which have but a comparatively slight effect on the stability of the peroxide at ordinary temperatures, decompose it vigorously at 98°. The cause of the catalytic decomposition of hydrogen peroxide has also been the subject of a good deal of speculation. Thénard[2] was at first disposed to regard the decomposition of hydrogen peroxide by the metals and certain metallic oxides as due to electricity. Later,[3] however, he came to look upon it as an inherent chemical property of the peroxide itself, and associated its instability with that of such compounds as nitrogen trichloride and mercury fulminate. Berzelius,[4] who proposed the term "catalysis" for this and similar phenomena, defined a catalytic agent as one which, "merely by its presence and not through its affinity, has the power to render active affinities which at ordinary temperature are latent." Thus, whereas Thénard considered the decomposition as brought about by chemical forces, Berzelius looked upon it as simply a contact action.

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[1] J. prakt. Chem., 1848–1868; Pogg. Ann.; Ztschr. f. Biol., **3**, 140, 325 (1867); see also Schaer: Ztschr. f. Biol., **37**, 320 (1899). A good summary of Schönbein's work is given by Bodländer, "Ueber langsame Verbrennung," in Ahren's "Sammlung chemischer und chemisch-technischer Vorträge," 1899.

[2] Ztschr. physiol. Chem., **16**, 340 (1892).

[3] Pflüger's Archiv., **67**, 615 (1897).

[4] Archiv. der Physiologie, [5], **8**, 311 (1896).

[5] Virchow's Archiv., **147**, 1 (1897).

[6] U. S. Dept. Agr. Rept., No. 68 (1901).

[7] Ztschr. phys. Chem., **31**, 258 (1899); **37**, 1, 323 (1901).

In 1839 De la Rive[5] advanced the theory of alternate oxidation and reduction of the platinum in order to account for its power to induce oxidations. According to this hypothesis, the action of finely divided platinum is analogous to that of nitric oxide in the production of sulphuric acid from sulphur dioxide and air.

The results of Helmholtz[6] and of E. von Meyer[7] have, however, been construed to indicate that De la Rive's hypothesis is untenable. As already pointed out above, Bredig and von Berneck[8] have carefully followed the catalytic decomposition of the peroxide by colloidal platinum, and have found the reaction to conform to the logarithmic equation for reactions of the first order: $\log \frac{1}{1-x} = 0.4343\, a\theta$. From this they have argued that only one molecule of the peroxide enters into the reaction, and that the reaction should, therefore, be represented by the equation:

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[1] This JOURNAL, **26**, 518 (1901).

[2] Ann. chim. phys., **9**, 94, 314 (1818).

[3] *Ibid.*, **9**, 441 (1818).

[4] Jsb., **15**, 237 (1836).

[5] Pogg. Ann., **46**, 489 (1839).

[6] *Ibid.*, **150**, 483 (1873); see Hüfner: J. prakt. Chem., [2], **10**, 385 (1874).

[7] J. prakt. Chem., [2], **14**, 124 (1876).

[8] Ztschr. phys. Chem., **31**, 258 (1899).

$$H_2O_2 = H_2O + O \quad \text{and not} \quad 2H_2O_2 = 2H_2O + O_2.$$

It is evident, however, from the development of the logarithmic equation that it can throw no light on the above question, nor can it show whether the metal enters chemically into the reaction provided it is again liberated during the process. By proving that a reaction conforms to the logarithmic equation, one merely shows that during the process the active mass of only one substance is altered. This is its limitation, and hence the work of Bredig and von Berneck throws no light on the question whether one or two molecules of hydrogen peroxide react, nor does it prove or disprove whether the metal effects the decomposition by undergoing alternate oxidation and reduction, since in this case the active mass of the metal, after the first instant, would remain unchanged throughout.

One of the most interesting observations on the decomposition of hydrogen peroxide by various organic and inorganic catalyzers is that certain substances, especially those of a highly poisonous nature, greatly inhibit the change, even when present in very small quantities. In this connection Schönbein was the first to call attention to the inhibiting action of hydrocyanic acid. He showed, in the most striking way, that hydrocyanic acid prevents the catalytic decomposition of hydrogen peroxide by the leaves of the *Leontodon* and also by the red-blood corpuscles.[1] He reached the conclusion, therefore, that sudden death as the result of hydrocyanic acid poisoning is due to an incapacitation of the red blood corpuscles, as the result of which suffocation is produced. From the fact that hydrocyanic acid inhibits the decomposition of hydrogen peroxide by both platinum and blood, Schönbein thought that the catalytic action of these two substances on the peroxide must be similar.

Bredig and his co-workers[2] have recently made an extensive study of the inhibitory action of many substances on the decomposition of the peroxide by colloidal platinum and gold. In this connection they have pointed out a number of interesting analogies between the colloidal metals and the enzymes, and have even gone so far as to call the colloidal metals "inorganic ferments." They carry the analogy further and speak of the action of inhibitors as "poisoning" the platinum. This analogy between the action of inhibitors on the catalytic decomposition by tissue extracts and by colloidal platinum is considered by them to be a most significant fact. They have shown, however, that in a few instances, substances which had been found not to inhibit the catalytic decomposition by tissue extracts do inhibit the action of colloidal platinum.

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[1] Ztschr. für Biol., 3, 140 (1867).

[2] Bredig and von Berneck: Ztschr. phys. Chem., 31, 258 (1899); Bredig and Ikeda: *Ibid.*, 37, 1 (1901); Bredig and Reinders: *Ibid.*, 37, 323 (1901).

On the other hand, our own results on the effect of various substances on the catalytic decomposition of hydrogen peroxide by different substances go to show that this analogy in the action of inhibitors on the catalysis, interesting though it may be, is still a mere coincidence, and that there are a number of substances which act altogether differently on the two orders of catalyzers, *i. e.*, they inhibit the one and accelerate the other.

As to the cause of the inhibitory effect of these several "poisons" on the decomposition of hydrogen peroxide by the colloidal metals, several theories have been advanced by Bredig and Ikeda, the substance of which is as follows:

1. The poison acts on the catalyzer and not on the hydrogen peroxide, at least such is the case with hydrocyanic acid.[1]

2. If it be assumed that for the catalytic decomposition of hydrogen peroxide, the presence of oxygen in the platinum is necessary, either dissolved or chemically united, then the effect of reducing substances, like hydrogen sulphide, hydroxylamine and phosphorus, is easily understood.

3. The surface of the platinum may be chemically or mechanically changed by the deposition of some layer, such as sulphur from hydrogen sulphide, and calomel or mercury from mercuric chloride.

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[1] In this connection see also Raudnitz: Ztschr. phys. Chem., **37**, 551 (1901).

4. The platinum may be chemically altered or dissolved, for example, by hydrocyanic and hydrochloric acids. The quantity of platinum present, however, is often far in excess of the "poisonous" substances.

5. The surface of the platinum may be so affected that the potential difference between it and the solution, and consequently its surface-tension, may be altered. This might be due to the formation of complex substances (such as $H_2Pt(CN)_4$) or to the removal of oxygen from the surface of the platinum by carbon.

It occurred to us in this connection that perhaps a better idea could be formed of the effect of various inhibitors on the catalytic decomposition of hydrogen peroxide by studying their effect on a number of substances capable of effecting the decomposition.

Accordingly, we have investigated the effect of a number of inhibitors on the catalytic decomposition by the following substances: Finely divided silver, platinum, copper, iron, silver oxide, thallium, ferrous oxide, copper sulphate, and catalase. Among the substances whose effect on the catalysis has been studied may be mentioned the following: Hydrocyanic acid, sodium nitrate, potassium nitrate, sodium chloride, sodium fluoride, sodium sulphate, sodium phosphate, sodium bicarbonate, potassium bromide, potassium oxalate, ammonium nitrate, ammonium chloride, ammonium sulphocyanate, thiourea, urea, hydrogen sulphide, hydroxylamine, phenylhydrazine, acetic acid, and sodium thiosulphate.

In order to determine the effect of these substances on the decomposition of hydrogen peroxide by the various catalyzers above mentioned, the following mode of procedure was adopted. A weighed amount of the catalyzer, usually 0.05 or 0.1 gram, was placed in a salt-mouth bottle, having a capacity of 200 cc. To this 1 cc. of a solution containing a known amount of the inhibitor was added. A small bottle of 6 cc. capacity, containing 5 cc. of 3 per cent hydrogen peroxide, was then carefully placed in an upright position in the larger bottle. The larger bottle was then connected with a gas-burette, and at a given instant the smaller bottle containing the hydrogen peroxide was overturned and the whole well shaken so as to intimately mix the contents. The solution of the inhibitor was thereby reduced to one-sixth of its original concentration. Readings were then made on the gas-burette at intervals of fifteen seconds. When not stated to the contrary, all observations were made at room temperature; and, inasmuch as small differences in the quantities of gas are not taken into account in the interpretation of our results, no corrections were made for the effect of temperature and pressure on the volume of the gas. In all of our experiments "Oakland, 3 per cent, Hydrogen Dioxide" was employed. This preparation now goes by the trade name of "Dioxogen." It has been found to be stable under ordinary conditions, very uniform in composition, and to contain no impurities that would interfere with our work. In order to make correction for any slight alteration in the strength of the peroxide solution while in use and for any variation in the temperature of the laboratory, control experiments with 1 cc. of water instead of 1 cc. of the solution of the inhibitors, were always tried at the beginning of every series of experiments with any given catalyzer, and in the event that any given series of experiments occupied us the entire day, several control experiments were tried at different intervals.

The finely divided silver used in our experiments was prepared by precipitating the metal from solutions of silver nitrate with finely powdered magnesium. The precipitated metal was treated with dilute nitric acid to remove small amounts of magnesium. It was then repeatedly washed with large amounts of water and dried at 75°. It was then rubbed in an agate mortar to a perfectly homogeneous powder.

In Table I. are given the results showing the effect of several neutral salts, urea, thiourea, hydrogen sulphide, hydroxylamine, and phenylhydrazine on the decomposition of the peroxide by finely divided silver.[1]

This series of experiments reveals many interesting facts.

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[1] In order to see the effect of any substance on the catalysis, compare the number of cubic centimeters of oxygen obtained with the volume of oxygen obtained in the control experiment for the same interval.

Table I.

0.1 gram silver. 5 cc. H_2O_2. 1 cc. water or solution.

Time. Sec.	1. Water.	2. N. $NaNO_3$.	3. N. NaCl.	4. N/10 Na_2F_2.	5. N. Na_2SO_4.	6. N/2. Na_2HPO_4.	7. N. $NaHCO_3$.	8. N. KNO_3.	9. N. KBr.	10. N/10 KBr.	11. N/100 KBr.	12. N/50 KI.
15	3.5[1]	5.5	0.25	11.0	8.0	4.0	6.0	6.0	0.0	0.0	1.5	0.75
30	6.5	10.0	1.75	14.0	15.0	6.0	8.5	11.0	0.0	0.0	4.0	1.25
45	10.0	14.0	5.00	17.0	22.0	7.5	12.5	13.75	0.0	0.5	7.5	2.0
60	13.0	17.5	9.00	20.0	29.0	9.0	16.0	16.00	0.0	0.5	10.0	3.0
75	15.75	20.5	12.00	22.0	34.0	10.5	19.5	19.00	0.0	0.5	12.0	4.5
90	18.25	22.75	13.50	24.0	37.0	12.0	22.0	21.75	0.0	1.0	14.0	6.0
105	20.00	24.50	15.50	26.0	39.0	13.25	24.5	24.00	0.0	1.5	17.0	7.5
120	21.50		17.00	28.0	41.0	14 5	26.5	25.75	0.0	1 5	19.0	9.0
135	22.75		18.50	29.5	43.0	15.3	28.5	27.50	0.0	2.0	20.75	10.8
150	23.5		20.5	30.5	44.0	16.25	30.25	28.50	0.0	2.0	22.75	12.3

Time. Sec.	13. N. $(COOK)_2$.	14. N. NH_4NO_3.	15. N. NH_4Cl.	16. N. NH_4CNS.	17. N/5 Thiourea.	18. N/5 Urea.	19. 0.6 N. H_2S.	20. 0.06 N. H_2S.	21. N/10 NH_2OH.	22. N/5 Phenylhydrazine acetate.	23. N/5 Acetic acid.
15	5.5	7.0	1.0	1.0	1.5	4.0	0.5	4.0	6.0	1.0	3.0
30	8.5	11.0	1.5	1.0	1.5	7.0	0.5	6.0	16.0	1.5	7.5
45	11.0	14.0	1.5	1.25	1.5	8.5	0.5	8.0	25.0	1.7	12.5
60	13.5	17.0	1.5	1.25	1.5	10.0	1.0	9.8	31.0	2.0	19.0
75	17.0	19.5	1.5	1.25	1.5	12.0	1.0	11.0	35.5	2.4	25.5
90	20.5	21.5	1.5	1.25	1.5	14.0	1.0	12.7	40.0	2.5	30.5
105	23.0	23.0	1.5	1.25	1.5	15.25	1.0	14.3	43.0	2.7	35.0
120	25.5	25.5	1.5	1.25	1.5	16.5	1.0	15.8	44.5	3.0	38.5
135	27.0	28.0	1.5	1.25	1.5	17.8	1.0	17.0	47.0	3.2	41.8
150	29.0	30.0	1.5	1.5	1.5	19.0	1.0	18.2	48.7	3.4	44.0

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[1] The numbers given under each column of the table represent the number of cubic centimeters of oxygen evolved in the given time.

The results obtained with the neutral salts indicate that those salts whose constituent acid yields an insoluble silver salt, inhibit the catalytic action of silver. Thus sodium chloride, ammonium chloride, and potassium bromide greatly inhibit, or really in the case of the two latter salts when acting in N/6 solution, practically prevent the decomposition by silver. This naturally suggested that the cause of the inhibition of the catalytic decomposition by various substances is due to the formation of an insoluble compound as a result of the action of the inhibitor on the catalyzer, whereby the latter becomes coated over with a thin, inpenetrable film of some insoluble substance. We are, however, apt to think of silver as much too inert to effect the decomposition of such salts as potassium bromide and sodium chloride under the conditions of the experiment.

On the other hand, it was long ago pointed out by Proust[1] that silver coins that had lain for many years under the sea were completely transformed into chloride. Then, too, it should be borne in mind that these metals in a fine state of division are much more active than in their ordinary form, and in this connection it has been observed that when finely divided silver is shaken with a neutral solution of potassium bromide or iodide the solution becomes alkaline to both litmus and phenolphthalein. This could only occur as the result of the formation of the silver halide. By comparing colums 3 and 15 of Table I., it will be observed that ammonium chloride is a much better inhibitor than sodium chloride. This is very satisfactorily explained by the fact that ammonium has less affinity for chlorine than sodium, and hence is much more easily replaced by silver, and therefore forms the insoluble coating of silver chloride much more readily with the sodium chloride. This view is still further strengthened by the fact that sodium fluoride has no inhibitory effect on the decomposition, the explanation being that silver fluoride is soluble. The same reasoning applies to the nitrates, sulphates and oxalates, etc.

The theory of the formation of an insoluble film also adequately explains how certain substances, even when acting in very small quantities, prevent the decomposition by much larger amounts of metal than they could possibly combine with.

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[1] Roscoe and Schorlemmer: "Treatise on Chemistry," Vol. II., Part I, 370, (1886).

The fact that potassium iodide (12) does not completely inhibit the catalytic action is explained by the fact that this salt is itself an active catalyzer. Hence the decomposition here noted is due almost, if not entirely, to the action of the salt itself, a fact that must be taken into consideration in all experiments in which this substance was used.

The inhibitory action of hydrogen sulphide (19 and 20) is also readily explained on the supposition that an insoluble film of silver sulphide is formed over the surface of the metallic silver.

The action of ammonium sulphocyanate as an inhibitor is peculiar and full of interest. In the first place it should lend itself readily to the formation of an insoluble coating of silver sulphocyanate. This alone would account for its powerful inhibitory effect. We have found, however, in addition to this, that this substance is very readily oxidized by hydrogen peroxide even in the cold and in the absence of an oxygen carrier, with considerable evolution of heat and the production of acid ammonium sulphate and hydrocyanic acid. Hence the loss of hydrogen peroxide, due to the oxidation of the sulphocyanate, together with the production of hydrocyanic acid, doubtless contributes to its apparent inhibitory effect. The interesting results obtained with this substance led us to try the action of its isomer, thiourea, and to compare this with urea. As seen in column 17, thiourea acts as powerfully on silver as an inhibitor as ammonium sulphocyanate. In this case there was apparently no oxidation, or at least no production of hydrocyanic acid. As yet we have not had time to study its action more fully and hence, at present, we are unable to completely explain its inhibitory effect. It may react with the metal to form a sulphide, or its tautomer may form an insoluble silver compound. Urea, on the other hand, showed only a very slight inhibitory effect, thus indicating that the inhibitory action of thiourea is in some way connected with the sulphur which it contains.

The inhibitory action of phenylhydrazine acetate (22) is very marked, whereas hydroxylamine (21) noticeably accelerates the decomposition. Tanatar[1] has recently studied the catalytic decomposition of hydroxylamine by finely divided platinum. It should be mentioned here that, under the conditions of our work, control experiments showed that there was no decomposition of the hydroxylamine.

In view of the fact that so many substances inhibit the catalytic decomposition of hydrogen peroxide by finely divided silver, the acceleration of this process by many neutral salts, such as the nitrates, fluorides, oxalates, and sulphates of the alkali metals and ammonium (see columns 2, 4, 5, 8, 13, and 14, Table I.), is exceedingly interesting. Obviously it is an altogether different phenomenon from the inhibition and some new factor must enter here. The inhibitor acts upon the catalyzer, whereas, on the other hand, it is probable that the accelerator combines with the hydrogen peroxide to produce very unstable addition-products, upon which the catalyzer can react more readily than upon the hydrogen peroxide alone. In this connection Engler and Nasse,[2] and also Schöne[3] and others, have observed that hydrogen peroxide is slowly decomposed by such salts as the chlorides of sodium, potassium and calcium, and sodium sulphate. Another fact of considerable interest might be mentioned in this connection, and that is, that in almost every case we were able to predict whether a given substance would accelerate or retard the catalysis by metallic silver, by reason of the fact that when treated with water or a solution of an accelerator, such as potassium nitrate or sodium sulphate, the silver was not wetted by the liquid and in part, at least, remained floating on the surface thereof. On the other hand, solutions of inhibitors were found to wet the silver at once, and caused it to sink to the bottom of the liquid, indicating that the surface of the metal had been changed in some way.

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[1] Ztschr. phys. Chem., **40**, 475 (1902).

[2] Ann. Chem. (Liebig), **154**, 231 (1870).

[3] *Ibid.*, **193**, 241 (1878).

Table II.—Effect of Hydrocyanic Acid on the Catalytic Decomposition by Silver.

0.1 gram Ag. 5 cc. H_2O_2. 1 cc. water or HCN.

Time. Sec.	1. Water.	2. N/5 HCN.	3. N/10 HCN.	4. N/20 HCN.	5. N/50 HCN.	6. N/100 HCN.	7. N/500 HCN.	8. N/1000 HCN.	9. N/2000 HCN.	10. N/5000 HCN.
15	4.7	1.0	1.5	2.0	3.5	4.0	4.5	4.25	4.0	7.7
30	9.0	1.5	1.5	3.75	5.0	5.5	7.0	7.0	7.5	12.5
45	12.5	1.5	1.75	4.5	6.5	7.0	9.0	9.25	10.0	14.87
60	15.0	1.75	1.75	5.5	7.25	8.0	10.5	11.0	12.0	19.0
75	17.6	1.75	2.0	6.5	8.0	9.0	12.0	12.75	14.0	21.62
90	20.0	2.0	2.5	7.5	9.0	10.0	13.5	14.25	15.5	23.87
105	22.0	2.0	3.25	8.5	10.0	11.0	14.5	16.0	17.0	26.12
120	23.8	2.0	4.5	9.25	10.5	12.0	15.5	17.25	18.5	27.62
135	25.5	2.0	5.5	10.0	11.4	12.9	16.4	19.0	20.0	29.62
150	27.0	2.25	6.25	10.5	12.4	13.5	17.4	20.0	21.25	31.25

Table III.—Silver.

Varying quantities of Ag. 5 cc. H_2O_2. 1 cc. H_2O or solution.

Time. Sec.	1. 0.05 gram Ag. 1 cc. water.	2. 0.1 gram Ag. 1 cc. water.	3. 0.2 gram Ag. 1 cc. water.	4. 0.4 gram Ag. 1 cc. water.	5. 0.05 gram Ag. 1 cc. N/10 KBr.	6. 0.1 gram Ag. 1 cc. N/10 KBr.	7. 0.2 gram Ag. 1 cc. N/10 KBr.	8. 0.4 gram Ag. 1 cc. N/10 KBr.	9. 0.8 gram Ag. 1 cc. N/10 KBr.
15	1.75	3.4	6.0	10.0	0.0	0.5	0.0	0.75	0.75
30	3.2	6.1	11.0	15.5	0.0	0.5	0.0	1.0	2.0
45	4.75	8.5	14.5	19.0	0.0	0.5	0.0	1.75	16.0
60	6.5	10.8	18.0	23.5	0.0	0.75	0.5	5.0	27.0
75	7.8	13.0	21.0	27.5	0.0	0.75	1.0	13.0	32.0
90	9.0	14.8	23.5	30.5	0.0	1.0	1.75	20.0	39.0
105	10.4	16.2	26.0	33.0	0.0	1.2	2.50	25.5	43.0
120	11.6	17.6	27.5	35.0	0.0	1.3	3.25	29.75	47.5
135	13.1	18.7	29.0	37.0	0.5	1.3	4.50	32.75	50.0
150	14.5	19.6	30.5	38.7	0.5	1.5	6.50	35.0	51.4

Table IV.

0.1074 gram silver oxide. 5 cc. H_2O_2. 1 cc. water or solution.

Time. Sec.	1. Water.	2. N/10 Na_2F_2.	3. N. NaCl.	4. N. KBr.	5. N. KI.[1]	6. N. KNO_3.	7. N. NH_4CNS.	8. N/5 HCN.	9. N/10 HCN.	10. N/50 HCN.	11. N/1000 HCN.
15	51.0	52.0	25.0	3.5	7.0	50.0	2.5	2.0	5.5	16.0	39.0
30	59.5	59.5	34.0	7.0	9.5	58.0	3.0	3.5	9.0	25.0	55.0
45	60.0		40.0	8.0	11.5		3.25	4.5	12.0	29.5	58.0
60			44.0	8.5	13.5		3.5	5.75	14.75	32.0	
75			46.0	9.25	14.25		3.75	7.5	17.0	34.0	
90			48.0	10.0	16.5		4.0	8.5	19.5	36.0	
105			49.5	10.5	17.5		4.0	9.75	21.5	37.0	
120			50.5	10.75	19.0		4.0	11.0	23.5	38.25	
135			52.5	11.25	20.0		4.0	12.0	25.5	39.0	
150			54.0	11.50	21.25		4.0	13.0	27.0	39.75	

[1] Liquid contained free iodine and became quite alkaline.

Table II shows the effect of varying quantities of hydrocyanic acid on silver. So much has been done already on the action of this inhibitor that but little need be said here. However, it will be noted that the hydrocyanic acid, when acting in N/12000 solution, possesses a very definite inhibitory action. It is of interest to note, however, that when acting in N/30000 solution it slightly accelerates the decomposition. A similar result was obtained by Bredig and von Berneck.[1]

The results given in Table III. show the effect of a constant quantity of potassium bromide on the catalysis by increasing amounts of silver, the hydrogen peroxide remaining the same in each experiment. It will be observed that while 1 cc. of N/10 potassium bromide almost completely checked the decomposition by 0.05 or 0.1 gram of silver, it is entirely inadequate to prevent the catalysis by 0.4 gram of silver, its retarding effect with this quantity being very marked only at first.

In the series of experiments given in Table IV, 0.0174 gram silver oxide was used, this being equivalent to the 0.1 gram of silver. The oxide is a much more powerful catalyzer than the metal. These experiments show that inhibitors affect similarly the decomposition by silver oxide and silver, and that they stand in the same order of efficiency. In the case of silver oxide, however, the inhibition is never so complete as in the case of silver. Thus potassium bromide, when acting in N/6 solution, altogether prevented decomposition of the peroxide by silver (Table I., column 9), whereas with the equivalent amount of silver oxide 11.5 cc. of oxygen were liberated in one hundred and fifty seconds. If as observed by Thénard, the oxide had been reduced to silver according to the equation,

$$Ag_2O + H_2O_2 = Ag_2 + H_2O + O_2,$$

10.4 cc. of oxygen under standard conditions would have been liberated, while the observed uncorrected volume was 11.5 cc. Hence most of the oxygen obtained probably resulted from this reduction.

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[1] *Loc. cit.*, Table 29, pp. 330 331.

The effect of these several substances on platinum has also been studied.

The platinum used in our work was prepared by precipitating the metal from a solution of platinum chloride by means of powdered magnesium. It was washed first with dilute sulphuric acid and then with water until the washings contained no sulphate. It was then dried at 85° and rubbed to a homogeneous powder.

0.05 gram of platinum was used in all of our experiments with this metal, otherwise the conditions of the experiments were essentially the same as those on the catalytic decomposition by silver. The results obtained with platinum are given in Table V.

It will be observed that finely divided platinum decomposes the peroxide much more rapidly than silver. It will also be observed that potassium bromide and iodide, and to a much less extent sodium chloride, retard the decomposition. The explanation is probably to be found in the fact that the platinous salts of the halogen acids are also insoluble. An experiment similar to that already described in connection with silver, demonstrated that the addition of finely divided platinum to a neutral solution of potassium bromide or iodide causes the solution to become alkaline. We would, therefore, have produced a thin film of insoluble platinous bromide or iodide over the surface of the metal by the action of this metal on these salts. Such a reaction as this, in which a comparatively inactive metal like platinum replaces a very powerful one like potassium in certain of its compounds, serves to illustrate the effect of the state of aggregation on the chemical activity of the reacting substance.

It will be observed that sodium fluoride does not retard the catalytic decomposition of the peroxide by platinum. While no reliable data are at present available on the solubility of platinous fluoride, we would naturally expect it to be soluble, and hence no protecting film of platinum fluoride would be formed over the surface of the metal.

In their study of the catalytic decomposition of hydrogen peroxide by colloidal platinum, Bredig and Ikeda obtained

Table V.

0.05 gram platinum. 5 cc. H_2O_2. 1 cc. water or solution of substance.

Time. Sec.	1. Water.	2. N/10 Na_2F_2.	3. N. NaCl.	4. N. Na_2SO_4.	5. N/10. $Na_2S_2O_3$.	6. N. KNO_3.	7. N. KBr.	8. N. KI.	9. N/5 HCN.	10. N/500 HCN.	11. N/2000 HCN.	12. N. NH_4CNS.
15	38.0	44.0	29.0	40.0	32.0	35.0	13.0	24.0	4.0	36.0	40.0	2.5
30	47.0	54.75	42.5	51.5	41.0	43.0	20.0	33.0	6.5	48.0	50.0	3.0
45	49.5	57.5	49.0	57.0	46.0	45.0	24.0	38.0	8.0	51.0	54.9	3.5
60	51.0	57.75	52.0	58.3	49.5	48.5	26.5	42.0	9.0	53.0		3.75
75	53.5		54.0		51.0	51.0	28.0	45.0	10.0	55.0		4.0
90	54.5		55.0		51.75	52.5	31.0	47.0	11.0	56.25		4.0
105	55.25		55.5		52.5	53.0	33.25	48.5	11.75			4.25
120	55.75		56.0		53.75	53.8	35.0	49.5	12.5			4.4
135	56.0				54.0	54.3	36.4	50.5	13.0			4.5
150	56.0				54.5	54.8	37.5	51.0	13.5			4.75

Time. Sec.	13. N/5 NH_4CNS.	14. N/50 NH_4CNS.	15. N/500 NH_4CNS.	16. N/5 Thiourea.	17. N/50 Thiourea.	18. N/5 Urea.	19. 0.6 N H_2S.	20. 0.006 N H_2S.	21. N/10 NH_3OH.	22. N/5 Phenylhydrazine acetate.	23. N/5 Acetic acid.
15	4.0	10.0	30.0	3.0	6.5	32.0	14.0	50	22.0	3.2	32.0
30	6.0	17.0	41.5	4.0	12.0	42.5	28.0	61	38.0	5.0	58.0
45	6.8	22.0	45.5	4.75	16.0	48.0	39.0	62	48.0	6.0	63.5
60	7.5	25.5	49.0	5.75	19.5	51.5	47.0		53.0	6.8	64.5
75	8.25	28.0	51.0	6.5	22.5	53.0	52.0		56.0	7.8	
90	8.75	30.0	52.5	7.5	24.5	54.0	54.5		59.0	8.5	
105	9.2	31.5	53.5	8.0	27.0	55.0	56.0		60.5	9.0	
120	9.5	32.6	54.0	9.0	28.5	55.5	57.5			9.4	
135	9.75	33.8	54.5	9.5	30.0	55.75	58.5			9.8	
150	10.00	35.0	55.0	10.0	31.5	56.0	59.0			10.0	

results quite similar to those given above. They found, for example, that hydrochloric acid inhibited the decomposition, whereas nitric acid accelerated it. In this connection they state: "Es ist also das Cl-ion der Salzsäure welches giftig wirkt. Da dieser auch in Chlorammonium enthalten ist, so zeigt sich dieses physiologisch wohl ziemlich harmlose Salz als ein wirkliches Platingift."[1] They think it likely that hydrochloric acid and its salts act by a formation of chlorplatinic acid, and state that the hydrogen peroxide acts on the hydrochloric acid forming free chlorine. Hence, according to these observers, the "poisoning" of the platinum is due to free chlorine, "which is also a strong poison for organisms." According to our view the inhibiting effects of hydrochloric acid, chlorides, bromides, and iodides depends upon the fact that the platinous halides are insoluble in water and that the platinum becomes covered over with an insoluble film.

Bredig and Ikeda also found that iodine powerfully inhibits the decomposition by platinum. They state that if the effect of the iodine is due to its oxidizing action on the platinum, then bromine should be an even stronger inhibitor. They found, however, that bromine is a much less powerful inhibitor than iodine. This analogy between the platinous and silver halides explains their result, since we should expect platinous iodide to be formed more readily than platinous bromide. Hydrogen sulphide, thiourea, and hydrocyanic acid did not inhibit the action of platinum as much as that of silver. That is what might be expected when we consider how much less readily platinum forms salts than silver.

Bredig and Ikeda found that hydroxylamine hydrochloride markedly inhibits the decomposition by colloidal platinum. As shown in Table V. (21), we found that free hydroxylamine caused some inhibition, but that the metal soon regained its original activity. In fact the decomposition was accelerated towards the close of the experiment.

The fact that in many respects thallium resembles silver, and that certain of the salts of these two metals exhibit analogous properties, rendered it important for our theory to test the conduct of this metal toward hydrogen peroxide. The thallous halides very closely resemble the corresponding silver salts in solubility and chemical conduct. Thus the fluorides of both metals are soluble in water, whereas the chlorides, bromides, and iodides of both are insoluble. On the other hand, these two metals display certain striking differences even in their -ous salts. Thus silver cyanide is insoluble in water, whereas thallous cyanide is quite soluble. It seemed, therefore, that with this metal an excellent opportunity was afforded of testing the truth of the ideas set forth above, respecting the action of inhibitors on the catalytic decomposition of hydrogen peroxide by metals.

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[1] *Loc. cit.*, p. 61.

Accordingly, the decomposition of the peroxide by thallium, acting alone and in the presence of various substances, has been studied. The softness of the metal, together with the fact that it oxidizes so easily on exposure to air, rendered it impossible to make use of the metal in the form of powder. Hence, thin shavings of it were employed, and inasmuch as it was found to break down hydrogen peroxide very slowly at ordinary temperatures, our experiments were performed at 40° C., at which temperature it decomposes the hydrogen peroxide quite actively. The results of our study of the catalytic action of thallium are given in Table VI.

It will be observed that the results reached with this metal are in perfect harmony with the theory, *viz.*, that the inhibition of the catalytic action is caused by the formation of a thin film of some insoluble substance over the catalyzer, this film being formed by the action of the catalyzer on the inhibitor. As shown in Table VI., potassium nitrate (2) and sodium fluoride (11) have no retarding effect on the decomposition, whereas potassium bromide (3 and 4), even when acting in N/60 solution, reduced it to a minimum. And, as was observed in the case of silver, ammonium chloride acted even more powerfully. The formation of the protective film on the surface of the thallium was proven by means of potassium bromide. It was observed that, on introducing a freshly-cut, lustrous piece of the metal in a normal solution of potassium bromide, it at once lost its luster and became covered over

Table VI.

0.1 gram thallium. 5 cc. hydrogen peroxide. 1 cc. water or solution. Temperature, 40° C.

Time. Sec.	1. Water.	2. N. KNO_3.	3. N. KBr.	4. N/10 KBr.	5. N/100 KBr.	6.[1] 0.83 N HCN.	7. N/10 HCN.	8. N. NH_4Cl.	9. N/100 NH_4Cl.	10.[2] N NH_4NO_3.	11. N/10 Na_2F_2.
15	3.0	5.5	0.75	0.0	1.5	0.5	1.8	0	3.8	2.5	4.0
30	14.0	26.5	0.75	0.5	5.5	1.8	6.0	0	24.0	7.5	19.0
45	29.0	52.0	1.0	0.5	14.0	4.2	12.5	0	50.0	11.8	42.0
60	46.0	59.8	1.0	0.75	28.5	6.0	18.0	0	60.5	15.2	56.8
75	57.0		1.0	1.0	47.0	7.7	25.0	0		18.0	59.6
90	59.0		1.0	1.25	58.0	8.8	31.0	0		20.1	
105	...		1.0	1.3	60.0	10.5	37.5	0		21.5	
120	...		1.0	1.6	...	11.5	43.5	0		22.7	
135							48.5			23.4	
150							52.5			24.4	
165							54.8			25.0	
180							56.0			25.7	

[1] All the metal was dissolved in this experiment except one small piece. Only a small quantity of thallic oxide was noted.

[2] Very little metal left at end of experiment.

with a white, opaque coating, and the solution became alkaline. We see, therefore, that the halides greatly retard the decomposition of hydrogen peroxide by both silver and thallium. On the other hand, the effect of hydrocyanic acid and ammonium nitrate on the catalytic decomposition of the peroxide by these two metals is markedly different. The catalytic power of silver is greatly lowered by the presence of minute quantities of hydrocyanic acid. Whereas, as may be seen from Table VI., column (6), hydrocyanic acid does not prevent the decomposition of the peroxide by thallium even when acting in about N/7 solution, and in the presence of N/60 hydrocyanic acid a brisk decomposition was observed. That hydrocyanic acid exerts any inhibitory effect whatsoever in the case of thallium is probably due to the fact that in the presence of the peroxide nearly all of the metal is dissolved and thus removed from the sphere of action. So also the retardation of the decomposition observed with ammonium nitrate is probably due to the fact that, in the presence of hydrogen peroxide and ammonium nitrate, practically all of the thallium is dissolved.

A study of the catalytic decomposition by copper and iron was undertaken for the reason that most of the salts of these metals are soluble. The copper used was prepared by sifting zinc dust into a copper sulphate solution and washing the precipitated copper with dilute hydrochloric acid, and then with water, until free from chlorides. It was then filtered and dried at 100 in a current of hydrogen. The iron employed in the experiments was the chemically pure reduced iron of Eimer and Amend.

The effect of inhibitors on the catalytic decomposition by copper and iron is much the same for both, and yet both differ markedly, with respect to the action of inhibitors, from any other metals thus far studied. It has been found, for example, that no substance completely inhibits the action of iron or copper when in the same concentration as employed in the experiments with the other metals.

Potassium bromide, which so powerfully inhibits the decomposition by silver and thallium, was found to have an ac-

Table VII.

0.1 gram copper. 5 cc. H_2O_2. 1 cc. H_2O or solution.

Time. Sec.	1. Water.	2. N/10 $Na_2S_2O_3$.	3. N. KNO_3.	4. N. KBr.	5. 0.6 N. H_2S.	6. N/5 HCN.	7. N. NH_4CNS.	8. N/5 Thiourea.	9. N/10 NH_2OH.	10. N/5 Phenylhydrazine acetate.	11. N/5 Acetic acid.
15	3.4	2.5	3.0	4.5	2.5	4.3	3.75	3.0	1.8	4.0	4.3
30	4.8	3.75	4.3	7.0	4.2	6.4	5.0	4.0	2.5	6.0	5.2
45	6.3	4.5	5.5	9.5	5.6	8.25	6.0	4.8	3.0	7.0	6.3
60	7.1	5.5	6.5	12.0	7.0	10.0	6.8	5.8	3.5	7.5	6.9
75	8.3	6.2	7.8	14.0	8.5	11.7	7.8	6.5	4.0	8.0	7.4
90	9.2	6.8	9.0	15.75	9.8	13.7	8.5	7.5	4.5	8.6	7.9
105	10.1	7.7	10.0	17.5	11.0	15.4	9.5	8.3	4.9	9.2	8.4
120	10.9	8.2	11.0	19.0	12.3	17.2	10.2	9.3	5.5	9.5	8.8
135	11.7	8.7	12.0	21.0	13.2	18.0	11.0	10.0	5.9	10.0	9.3
150	12.5	9.3	12.9	22.25	14.1	20.3	11.8	10.8	6.2	10.3	

Table VIII.

0.1 gram iron. 5 cc. H_2O_2. 1 cc. H_2O or solution.

Time. Sec.	1. Water.	2. N. KBr.	3. N. NH_4CNS.	4. N/5 HCN.	5.[1] 1 cc. water.	6. N. NH_2OH	7. N/5 Phenylhydrazine acetate.	8. N/5 Acetic acid.
15	3.7	3.5	1.5	5.8	1.75	1.5	1.5	1.5
30	5.7	5.5	2.0	9.8	2.8	2.0	2.2	2.2
45	7.4	7.5	2.9	13.0	3.5	2.4	3.2	3.0
60	8.9	9.5	3.8	15.9	4.2	2.8	3.7	3.5
75	10.3	11.0	4.4	18.6	5.0	3.2	4.5	4.0
90	11.6	12.8	5.0	20.8	5.6	3.5	5.4	4.5
105	12.9	14.7	6.5	22.9	6.3	3.8	5.9	5.0
120	14.0	16.4	7.0	24.8	6.8	4.1	6.5	5.5
135	15.1	17.8	7.5	26.4	7.5	4.5	7.0	6.1
150	16.1	19.5	8.25	27.8	8.1	4.8	7.5	6.5

celerating effect on the action of both copper and iron. Hydrocyanic acid, which has been found to inhibit the decomposition by all substances previously studied, both organic and inorganic, was found to cause a marked acceleration in the action of copper and iron. This fact was of sufficient interest to warrant further study. In order to bring out to better advantage the accelerating action of hydrocyanic acid, the following experiments were tried at 60° :

Copper.

0.1 gram Cu. 5 cc. H_2O_2. 1 cc. water, or N/10 HCN.
Temperature, 60°.

Time in minutes.	1 cc. water.	1 cc. N/10 HCN.
0.5	13.0	28.0
1.0	32.5	44.0
1.5	42.0	49.8
2.0	46.2	51.9
3.0	50.0	53.0
4.0	51.6	53.1
5.0	52.3	53.1

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[1] The reduced iron used in Experiments 5, 6, 7, and 8 had stood exposed to the air for several days, hence the falling off in catalyzing power as compared with that used in Experiments 1, 2, 3, and 4.

Iron.

0.1 gram Fe. 5 cc. H_2O_2. 1 cc. H_2O, or N/10 HCN.
Temperature, 60°.

Time in minutes.	1 cc. water.	1 cc. N/10 HCN.
0.5	3.8	29.0
1.0	11.5	43.0
1.5	18.3	46.0
2.0	24.0	48.1
3.0	31.2	49.3
4.0	36.1	49.8
5.0	46.3	50.1

These experiments prove that hydrocyanic acid greatly accelerates the decomposition of the peroxide by both copper and iron, especially in the earlier stages of the reaction, the amount of oxygen liberated by the copper in the first half minute being doubled by the presence of the hydrocyanic acid, and in the case of iron the rate of decomposition is increased over seven times.

We have also observed that hydrocyanic acid greatly accelerates the rate of decomposition of hydrogen peroxide by ferrous hydroxide at ordinary temperatures, and at the same time the course of the reaction of hydrogen peroxide on ferrous hydroxide is very materially changed by the presence of hydrocyanic acid. The difference in the two reactions is certainly very striking. On adding hydrogen peroxide to ferrous hydroxide alone, the latter is oxidized to the ferric condition at once with but little or no decomposition of the peroxide. On the other hand, when N/5 hydrocyanic acid is added to the ferrous hydroxide, and then hydrogen peroxide, the mixture takes on the color of Prussian blue, and simultaneously a vigorous decomposition of the hydrogen peroxide occurs. Here the acceleration produced by the hydrocyanic acid is a distinctly chemical effect and is easily explained by the formation of one of the double cyanides of iron, probably Prussian blue, all of which have been found to decompose hydrogen peroxide at ordinary temperatures.

A reaction somewhat similar to this has been observed in studying the decomposition of hydrogen peroxide by copper sulphate at high temperatures. Here, as has been observed with the ferrous hydroxide, the decomposition of the peroxide is greatly accelerated by hydrocyanic acid, due doubtless to the formation of cupric or cuprous cyanide and its action on the peroxide. The exact amount of this acceleration may be seen from the following :

Table IX.—Effect of Hydrocyanic Acid on the Catalytic Decomposition of Hydrogen Peroxide by Copper Sulphate at 85° C.

Conditions.	Time. Min.	I. Water. cc.	II. N/10 HCN. cc.	Remarks.
I. 5 cc. N H_2O_2	1	11.5	46.5	
4 " H_2O	.	...	...	
1 " N/20 copper sulphate	2	24.5	52.5	
II. 5 cc. N H_2O_2	3	32.8	53.5	A light green flocculent precipitate is produced in Exp. II.
1 " N/10 HCN	4	38.5	54.3	
3 " H_2O	.	...	...	
1 " N/20 copper sulphate	5	42.0	54.3	

It yet remained to test the effect of the inhibitors employed in this investigation on the catalytic decomposition of hydrogen peroxide by catalase. As a convenient source of animal catalase the liver of the hog was chosen. A 10 per cent aqueous extract of the liver was prepared by macerating it thoroughly with coarsely powdered glass, adding the required amount of water, and straining through cloth. In the series of experiments with phenylhydrazine, an extract of liver was employed that had stood over night with toluene. During this interval a coagulum was formed. This was filtered off and the clear yellow extract used in the three series of experiments, the results of which are given in columns 19, 20, and 21 of Table X.

In the other experiments on catalase, the extract of liver was used on the day that it was prepared. The experiments with liver catalase were carried out in the following manner :

One cc. of the liver extract and 1 cc. of water, or of the solution of the substance whose effect on the catalase was to be tried, were placed in the larger bottle. The small bottle, containing 5 cc. of hydrogen peroxide, was carefully introduced. The large bottle was then connected with the gas-burette, and when everything was in readiness, the small bottle was overturned and its contents mixed with that in the larger bottle. The oxygen evolved was then read off at intervals of fifteen seconds until the experiment was brought to a close. In order to obtain comparable results it was found necessary to continually shake the large bottle during the experiment. Loew also found this to be necessary, The experiments were performed at room temperature.

Our results with catalase are given in Table X.

An examination of these results goes to show that the effect of these several substances on the catalytic decomposition of hydrogen peroxide by liver catalase is entirely different from that which they exert on the decomposition by finely divided metals. Catalase resembles silver, platinum and silver oxide, in that hydrocyanic acid (Table X., 17) strongly inhibits its action on the peroxide; on the other hand, it differs from copper, iron, and thallium in this respect. It resembles platinum also in that potassium bromide (8) does not completely inhibit its action on the peroxide. But it differs in this respect from silver and thallium on the one hand, and from copper and iron on the other, for the reason that this salt completely inhibits the action of silver and thallium, whereas it accelerates the decomposition of the peroxide by copper and iron. Next to hydrocyanic acid, hydroxylamine and the nitrates of sodium, ammonium, and potassium have been found to inhibit the action of catalase to the greatest degree (4, 10, 12, and 18). On the other hand, it has already been pointed out that these substances greatly accelerate the decomposition by silver. Thus hydroxylamine accelerates the action of silver 100 per cent, while it reduces the activity of liver catalase to 1/25 of its original value. Hydroxylamine and the nitrates have been found to have practically no influence on the decomposition of the peroxide by platinum. Similarly thiourea, which accelerates the decomposition by liver catalase, was found to reduce the activity of silver and platinum to 6 and 10 per cent of their former values, respectively.

Table X.

1 cc. liver extract. 5 cc. H_2O_2. 1 cc. water or solution.

Time. Sec.	1. Water.	2. N. NaCl.	3. N. Na_2SO_4.	4. N. $NaNO_3$.	5.[1] N. $NaNO_3$.	6. N/10 Na_2F_2.	7. N. $Na_2S_2O_3$.	8. N. KBr.	9. N. KI.	10. N. KNO_3.	11. N. NH_4Cl.
15	27.5	17.0	48.0	8.8	1.0	15.0	48.0	23.0	46.0	7.0	19.0
30	45.0	23.0	59.0	9.2	1.2	29.0	59.0	26.5	57.0	7.4	24.0
45	50.5	28.0	60.5	9.4	1.5	43.0	60.5	28.5	62.0	7.6	27.5
60	58.0	31.0	61.5	9.6	1.7	56.0	61.5	29.5	63.5	7.8	30.0
75	61.0	33.0		9.8	1.8	62.0		30.5	65.5	8.0	31.8
90	62.2	33.8		10.0	2.0	65.0		31.5		8.1	33.0
105	63.8				2.0			31.5		8.2	33.5
120					2.25					8.3	34.2
135					2.25					8.4	34.8
150					2.25					8.5	35.0

Time. Sec.	12. N. NH_4NO_3.	13. N/5 NH_4CNS.	14. N/5 Thiourea.	15. N/5 Urea.	16. 0.6 N. H_2S.	17. N/5 HCN.	18. N/10 NH_2OH.	19.[2] Water.	20. N/5 Acetic acid.	21. N/5 Phenylhydrazine acetate.
15	5.4	2.5	36.0	16.0	2.2	0.75	1.0	20.0	3.8	5.0
30	5.8	2.8	58.0	26.0	4.8	0.75	1.2	28.0	6.3	11.0
45	6.0	3.0	64.0	36.0	7.5	1.8	1.5	32.0	7.8	17.0
60	6.1	3.2		44.0	9.8	3.0	1.8	36.0	9.0	22.0
75	6.2	3.3		51.0	12.2	3.8	2.0	38.0	10.0	27.0
90	6.3	3.6		56.0	15.3	4.2	2.4	40.0	10.5	32.0
105	6.4	3.8		60.0	17.7	5.0	2.5	41.0	11.0	38.0
120	6.4	3.8		62.5	18.0	6.0	2.7	42.0	11.4	42.0
135	6.5	3.8			21.8	6.5	3.0	43.0	11.5	46.0
150	6.5	4.0			21.8	7.0	3.2	44.5	11.7	48.5

[1] The nitrate and the extract were mixed one hour before the series was taken.

[2] A different extract was used in columns 19, 20, and 21.

It is believed therefore that the facts set forth in the above justify the following conclusions:

1. That various catalyzers are affected differently by different substances,—some of the latter retarding, others accelerating the decomposition of hydrogen peroxide.

2. That the effect of any particular substance on the catalyzer, whether to retard or accelerate its action, can be explained, in the majority of cases at least, upon purely chemical grounds. The action of hydrocyanic acid on ferrous hydroxide in the presence of the peroxide is here cited as a case in point. This, of course, does not apply to the effect of accelerators and inhibitors on catalase. As the nature of this substance is still unknown, so the effect of these several substances upon it must be largely a matter of conjecture.

3. That the inhibitory effect of many substances on the catalytic power of the finely divided metals is due to the formation of a thin insoluble film of a compound of the metal over its surface, this compound being formed by the action of the metal on the inhibitor. This explains why a very small amount of the inhibitor will hold in check a much larger quantity of the metal.

4. Certain substances, like ammonium sulphocyanate, may inhibit the catalytic decomposition for several reasons: First, by being themselves oxidized by the hydrogen peroxide, and thus removing the latter from the solution; or, secondly, in their oxidation a substance like hydrocyanic acid may be produced which is capable of acting as an inhibitor in a manner already discussed above.

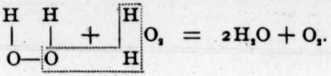
5. That the inhibiting action of various substances on the decomposition of hydrogen peroxide in no way indicates a real analogy between the inorganic and organic catalyzers.

ON THE OXIDATION OF FORMIC ALDEHYDE AND FORMIC ACID BY HYDROGEN PEROXIDE IN THE PRESENCE OF VARIOUS CATALYZERS. THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE AND INDUCED OXIDATION ARE CORRELATED PHENOMENA.

The oxidation of various substances by hydrogen peroxide, alone and in the presence of various catalyzers and oxygen carriers, has been made the subject of numerous and extended investigations since the discovery of the compound by Thénard. The results reached by Fenton[1] and others, in recent years, in the synthetic oxidation of many organic compounds through the use of hydrogen peroxide, in the presence of ferrous salts, have proved of the greatest possible interest and importance, and yet in spite of all that has been done in these various directions, but little has as yet been accomplished towards arriving at a clear conception of the mechanism of these oxidations.

The simplest view to take of the action of hydrogen peroxide as an oxidizing agent is that in any oxidation it is decomposed into water and active (atomic) oxygen, and that the oxidation is in reality brought about by this latter substance. From this it follows logically, therefore, that any substance that can effect the catalytic decomposition of the peroxide can also bring about oxidations that cannot be effected by hydrogen peroxide alone. The idea that hydrogen peroxide, when it decomposes, gives atomic oxygen as one of the products of decomposition, though an old one, has, as already pointed out above, been again brought forward recently by Bredig and von Berneck[2] in order to explain the results reached by them on the decomposition of the peroxide by colloidal metals.

On the other hand, Traube,[3] in his exhaustive researches on hydrogen peroxide, reached the conclusion that, on heating, the molecules of hydrogen peroxide decompose each other mutually; that two weakly held hydrogen atoms of 1 molecule of the peroxide split a second into two hydroxyl groups with the result that water is produced, and molecular or passive oxygen set free; thus, to use his method of representation:



$$\begin{array}{cc}H & H\\ | & |\\ O- & O\end{array} + \begin{array}{c}H\\ \\ H\end{array}O_2 = 2H_2O + O_2.$$

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[1] Fenton and Jones: J. Chem. Soc. (London), 77, 69 (1900).

[2] *Loc. cit.*

[3] Ber. d. chem. Ges., 26, 1476 (1893).

According to this way of looking at the decomposition of hydrogen peroxide, the mechanism of oxidations effected by means of it, and the accelerating effect of catalyzers on such oxidations, are by no means so easily explained as by the assumption that active oxygen is produced in its decomposition. However this may be, certain chemists have come to see the fallacy of the simpler explanation, and have been led to believe that it is not atomic oxygen produced in the decomposition of the hydrogen peroxide that effects the oxidation of a given substance by the peroxide, but rather the undecomposed portions of the hydrogen peroxide itself. In this connection Loew[1] states that there is no connection between the power of a substance to decompose hydrogen peroxide and that of causing the oxidation of guaiacum by means of the peroxide, and in support of this conclusion he cites the work of Lépinois,[2] who, two years previously, stated that there is not always a parallelism between the quantities of oxygen developed from hydrogen peroxide by the action of ferments and the intensity of other reactions, such as the oxidation of guaiacum and guaiacol. On the other hand, the views of Loew and Lépinois are opposed to the results of Spitzer,[3] who found that, with few exceptions, the various tissues decompose hydrogen peroxide in the same order that other investigators (Abelous and Biarnés, also Salkowski) had found them to oxidize salicylic aldehyde. Spitzer concluded, therefore, that the power of a tissue to decompose hydrogen peroxide is a true index of its oxidizing power.

From certain preliminary observations on the oxidation of certain substances by hydrogen peroxide, the writers of this communication had about reached the conclusion that hydrogen peroxide can only act as an oxidizing agent when it is not being actively decomposed by catalyzers into water and oxygen. In other words, that it is the hydrogen peroxide itself and not the oxygen resulting from its decomposition that effects the oxidation. It soon became evident, however, that certain substances, if not all, that act as oxygen carriers towards hydrogen peroxide also bring about the decomposition of at least a part of the peroxide catalytically, and, vice versa, that most substances, at least, that decompose hydrogen peroxide catalytically can also effect the oxidation of certain substances by means of hydrogen peroxide, that under ordinary conditions are not oxidized by this compound alone.

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[1] U. S. Dept. Agr. Rep., **68**, 12 (1901).

[2] Compt. rend. Soc. Biol., 1899, p. 401.

[3] Pflüg. Arch., **67**, 615 (1897).

In order, therefore, to form a better idea of the correlation existing between these processes, it was decided to study the effect of various catalyzers on certain oxidations capable of being effected by hydrogen peroxide. In this connection it occurred to us that possibly the oxidation of formic aldehyde by hydrogen peroxide might prove a suitable one for our purpose, for the reason that it had already been studied by us to some considerable extent,[1] and in some respects, at least, was fairly well understood.

In studying the effect of catalyzers on the oxidation of formic aldehyde by hydrogen peroxide, we made use of a simple piece of apparatus, recently described by Manchot and Herzog.[2] This apparatus, a cut of which is shown in Fig. I., was modified to the extent of using a small, thin-walled glass bottle instead of a flask, and by connecting the stop-cock of the separating-funnel rigidly to a piece of glass tubing (C), thereby enabling us to keep the entire apparatus immersed in a water-bath at any desired temperature, and allowing the two liquids to mix only when they and the entire apparatus had acquired the temperature of the bath. The apparatus was kept immersed in the bath by putting lead weights around the neck of the bottle. Normal formic aldehyde and normal hydrogen peroxide were employed, and, unless expressly stated to the contrary, 5 cc. of each of these solutions were used in each experiment. The formaldehyde was always put in the bottle along with the catalyzer, and the hydrogen peroxide in the separating-funnel. By opening the stop-cock the hydrogen peroxide was allowed to flow down and mix with the formic aldehyde, the duration of the experiment being counted from the moment the two liquids were brought to-

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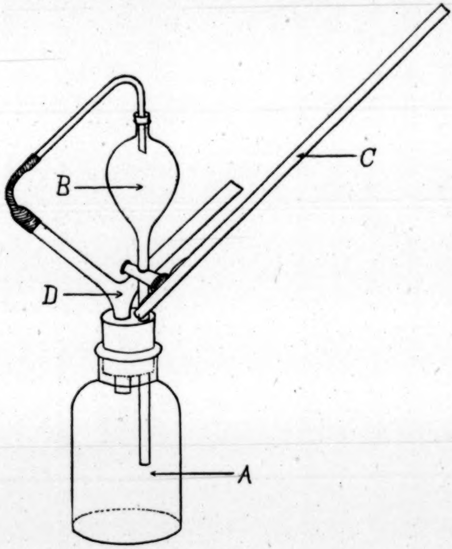
[1] J. Am. Chem. Soc., **21**, 262 (1899).

[2] Ann. Chem. (Liebig), **316**, 321 (1901).



gether. The apparatus was connected with a gas-burette in order to measure the amount of any gas produced during the experiment. The results of our experiments, together with the names and amounts of the several catalyzers employed, and also all other data necessary to a correct understanding of the work, are given in the following table. In each experiment 5 cc. of N. hydrogen peroxide and 5 cc. of N. formic aldehyde were used. The temperature in every case was 60° and the duration of each experiment was fifteen minutes.

Table I.

No. of experiment.	Catalyzer.	N/5 NaOH required. cc.	Gas evolved. cc.	Per cent of aldehyde oxidized to formic acid.
1	None	2.1	none	8.4
2	0.1 gram sugar charcoal	2.7	none	10.8
3	0.05 gram platinum black[1]	0.0	57.0	none
4	0.1 gram bone-black	12.2	24.0	48.8
5	0.05 gram platinum black[1]	0.2	54.5	none
6	0.1 gram animal charcoal	11.7	21.0	46.8
7	0.1 " " " 2d specimen	2.3	8.8	9.2
8	0.1 " ferric hydroxide[2]	3.1	22.7	23.6
9	0.1 " ferrous ammonium sulphate	10.10	7.0	66.8
10	0.01 " " " "	7.15	4.0	54.6
11	0.002 gram " " "	1.0	1.0	8.0
12	0.077 " ferric nitrate[3]	20.60	5.0	69.2
13	0.0077 " " "	5.9	9.10	21.0
14	0.0123 " " ammonium alum	3.9	4.0	12.60
15	0.0071 gram ferrous sulphate	19.3	7.0	74.80
16	0.0071 " " "	17.4	7.2	67.2
17	0.00139 " " "	2.55	4.1	10.2
18	0.00278 " " "	4.18	7.4	16.72
19	0.00417 " " "	5.00	5.1	20.0
20	0.00556 " " "	6.85	2.2	27.4
21	0.00695 " " "	17.08	5.7	68.36
22	0.0139 " " "	18.2	2.2	72.8

In looking over the results in Table I., on the effect of various substances on the oxidation of formic aldehyde by hydrogen peroxide, it seemed to us somewhat remarkable that as active a catalyzer as platinum black should have no effect on the oxidation, other than that of causing an apparent retardation. If such were really true, it would seem to support the conclusion that oxidations by hydrogen peroxide are brought about not by any oxygen liberated from the same but by means of the peroxide itself.

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[1] All of the hydrogen peroxide was used up in this experiment.

[2] Fe(OH)$_3$ alone was found not to oxidize formic aldehyde at this temperature.

[3] The acidity of all salts having an acid reaction was determined in every case on the quantity of the salt used in any given experiment, and a correction made on the N/5 NaOH required in each experiment.

However, in this connection, it was observed that platinum black accelerated the oxidation of guaiacum by hydrogen peroxide; and, further, that just as the catalytic decomposition of hydrogen peroxide is retarded by cold and accelerated by heat, so also the rate of oxidation of guaiacum by hydrogen peroxide in the presence of finely divided platinum was found to be dependent on the temperature, being more rapid the higher the temperature. This plainly indicated that in certain oxidations effected by hydrogen peroxide, platinum black plays the part of an oxygen carrier.

It therefore occurred to us that while formic acid is not oxidized by hydrogen peroxide alone at 60° to 80° C.,[1] it might be oxidized by it in the presence of certain oxygen carriers like spongy platinum, with the result that the formic acid produced by the oxidation of the aldehyde, might itself be oxidized to carbon dioxide and water as fast as formed, thereby completely obscuring the real carrying power of the platinum.

That both formic aldehyde and formic acid are oxidized by hydrogen peroxide under the influence of platinum black, and that formic acid is oxidized to far greater extent than the aldehyde, even when both are present together, may be gathered from the following experiments:

I. 5 cc. of a solution of formic aldehyde were mixed with 5 cc. of N. hydrogen peroxide. 5 cc. of this mixture taken out at once was found to have no increased acidity. This was then mixed with 22.75 cc. N. sodium hydroxide, and to this mixture 50 cc. of 3 per cent hydrogen peroxide were added.[2] After standing for some time this mixture was titrated with N. hydrochloric acid. It took 19.35 cc. N. hydrochloric acid. Hence to calculate the quantity of formic aldehyde present in the original mixture we have $22.75 - 19.35 = 3.4 - 1.2 = 2.2$, and $2.2 \times 2 = 4.4$ cc. N. sodium hydroxide required to neutralize all of the formic acid present. Hence 5 cc. formic aldehyde solution contain 0.1320 gram.

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[1] In our earlier work on the oxidation of formic aldehyde by hydrogen peroxide, we proved that formic acid is not oxidized by hydrogen peroxide at these temperatures. J. Am. Chem. Soc., **21**, 262 (1899).

[2] Fifty cc. of the 3 per cent hydrogen peroxide used in these determinations had an acidity equal to 1.2 cc. N. hydrochloric acid.

II. 5 cc. of the solution of formic aldehyde, together with 5 cc. of N. hydrogen peroxide were heated, at 60°, for fifteen minutes. The formic aldehyde remaining unoxidized under these conditions was determined in 5 cc. of the mixture by means of N. caustic soda and 3 per cent hydrogen peroxide with the following results:

Five cc. of the mixture with 50 cc. of hydrogen peroxide and 22.84 cc. N. caustic soda required, at the end of the oxidation, 19.55 N. hydrochloric acid. Hence $22.84 - 19.55 = 3.29 - 1.2 = 2.09 \times 2 = 4.18$ cc. N. caustic soda used to neutralize the formic acid produced by the oxidation of the formic aldehyde remaining in the mixture. Therefore the amount of formic aldehyde remaining in the mixture was 0.1254 gram. Hence 5 per cent of the formic aldehyde was oxidized under the conditions of the experiment.

III. 5 cc. of the formic aldehyde solution, with 5 cc. N. hydrogen peroxide were heated for fifteen minutes at 60° C., with 0.05 gram of platinum black. At the end of this time the mixture was filtered on a dry filter. The filtrate was neutral. The formic aldehyde remaining unoxidized was determined in the manner already described. Found, 0.08592 gram of formic aldehyde. Therefore, 0.04608 gram of formic aldehyde, or 34.9 per cent, had been oxidized under these conditions.

IV. In this experiment 5 cc. of the formic aldehyde solution, together with 5 cc. of N. formic acid and 5 cc. N. hydrogen peroxide, were heated for fifteen minutes at 60° C. with 0.05 gram platinum black. 86.7 cc. of gas were evolved in this experiment, and this gas was found to contain carbon dioxide. At the end of the experiment the mixture was filtered through a dry filter. Five cc. of the filtrate required 2.45 cc. N/5 sodium hydroxide to neutralize, hence the whole required 7.35 cc. of N/5 sodium hydroxide to neutralize the free acid left. The amount of formic aldehyde remaining was determined in the usual manner and found to be 0.1278 gram. Therefore, 0.0042 gram, or 3.1 per cent, of the formic aldehyde had been oxidized under these conditions. On the other hand, 70.49 per cent of the formic acid was oxidized under these conditions, as may be seen from the following: A mixture like that employed in this experiment of 5 cc. formic aldehyde, 5 cc. of N. formic acid, and 5 cc. of hydrogen peroxide required before the oxidation 24.9 cc. N/5 caustic soda, whereas, after such a mixture had been oxidized it required only 7.35 cc. N/5 caustic soda. Hence, 70.49 per cent of the acid had been oxidized under the conditions of the experiment.

Several interesting conclusions may be drawn from these experiments:

1. That in the absence of formic acid the oxidation of formic aldehyde by hydrogen peroxide is greatly accelerated by finely divided platinum.

2. That, whereas, formic aldehyde is much more easily oxidized by hydrogen peroxide alone than formic acid, the latter is about twice as readily oxidized as the former by hydrogen peroxide when platinum is present; and that when a mixture of the acid and aldehyde are present in equal quantities with spongy platinum and a quantity of hydrogen peroxide in quantity sufficient to oxidize either but not both, to the next higher state of oxidation, the acid is oxidized almost to the exclusion of the aldehyde.[1]

It was further evident from these results that formic acid would probably prove more useful in studying the effect of various catalyzers on the oxidation by hydrogen peroxide than formic aldehyde. Accordingly, the effect of a number of catalyzers was tried on the oxidation of formic acid by hydrogen peroxide, making use of the apparatus already described. Five cc. of N. formic acid were put in the bottle along with a weighed amount of the catalyzer; 5 cc. of N. hydrogen peroxide were placed in the separating-funnel. The whole apparatus was then immersed in a water-bath and allowed to come to the temperature of the bath, when the stop-cock was opened and the hydrogen peroxide allowed to mix with the acid and catalyzer, the duration of the experiment being counted from this instant. At the end of a given time, usually after the lapse of fifteen minutes, the apparatus was removed from the bath and cooled, and, when necessary, the contents filtered on a dry filter. Five cc. of the mixture were then titrated with N/5 caustic soda to determine the loss of acidity due to oxidation, and 1 cc. was titrated with permanganate in order to determine the quantity of hydrogen peroxide consumed in the oxidation. During the experiment the apparatus was usually connected with a gas-burette in order to determine the amount of gas evolved.

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[1] Van 't Hoff also seems to consider formic acid a stronger reducing agent than formic aldehyde, for the reason that it can reduce mercuric oxide, whereas the aldehyde cannot (Vorlesungen über theoretische und physikalische Chemie, 1900, p. 117).

The results obtained in this series of experiments, together with all essential conditions of the experiment, are given in Table II.

The effect of the several catalyzers is apparent from the results set forth in the above table. It will be observed that even at 97° C. the oxidation of formic acid by hydrogen peroxide alone amounts only to 5.6 per cent in fifteen minutes, whereas in the presence of small amounts of ferrous salt, copper sulphate, platinum black, and potassium iodide, the oxidation proceeds with great rapidity even at 60° C. It is interesting to note, in this connection, that those substances which exert this accelerating effect on the oxidation also decompose hydrogen peroxide under the same conditions, whereas substances like potassium chloride, which do not decompose the peroxide, do not accelerate the oxidation to any extent. This fact is certainly significant and suggestive, and is brought out in a very striking manner in the case of finely divided gold and platinum. At ordinary temperatures, finely divided gold decomposes a faintly acid solution of hydrogen peroxide very slowly indeed, whereas finely divided platinum effects the decomposition of the peroxide with great rapidity. So in the same way it has been found that at ordinary temperatures finely divided gold scarcely accelerates the oxidation of formic acid by hydrogen peroxide to a measurable extent in twenty-four hours, whereas finely divided platinum under the same conditions brings about the oxidation of 45.2 per cent of the acid present in two minutes. That such is the case may be seen from the following experiments :

I. 0.05 gram gold with 5 cc. N. formic acid and 5 cc. N.

Table II.

No. of experiment.	Catalyzer.	N. Formic acid used. cc.	N. Hydrogen peroxide used. cc.	Time. Min.	Temperature.	N/5 NaOH required.	KMnO₄ used.[7]	Gas evolved. cc.	Per cent oxidation.	Per cent of hydrogen peroxide decomposed.
1	None	5	5	15	60°	24.72	...	none	1.12	none
2[1]	0.05 gram platinum	“	“	“	“	9.5	none	86.2	62.0	100.0
3	0.00139 gram $FeSO_{47}.H_2O$	“	“	“	“	24.1	90.5	....	3.92	5.23
4	0.00278 “ “	“	“	“	“	23.58	86.0	....	5.68	9.94
5	0.00417 “ “	“	“	“	“	21.11	74.0	....	15.56	22.51
6	0.00556 “ “	“	“	“	“	18.95	57.0	....	24.2	40.31
7	0.00695 “ “	“	“	“	“	17.9	....	....	28.4	....
8	0.0139 “ “	“	“	“	“	9.1	....	....	63.6	....
9[2]	0.1 “ silver	“	“	“	“	19.5	....	....	22.0	....
10[3]	1 cc. N. KI	“	“	“	“	1.76	....	88.5	92.9	....
11	1 cc. N. KCl	“	“	“	“	24.31	....	0.75	2.8	....
12	None	“	“	“	90°	24.2	....	....	3.2	....
13	0.01 gram $CuSO_4.5H_2O$	“	“	30	“	12.45	17.5	68.8	50.2	81.67
14[4]	1 cc. 2/5 N. HI	“	“	15	“	19.94	....	9.8	20.24	....
15[5]	0.1 gram copper	“	“	“	“	10.2	2.0	81.1	59.2	97.90
16	None	“	“	“	97°	23.60	84.0	7.2	5.60	12.04
17[6]	0.05 gram gold	“	“	“	“	40.3	35.0	54.0	19.4	63.35
18	“ “ “	“	“	“	“	20.0	58.5	30.7	20.0	38.74

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[1] In Experiments 2, 4, 7, 9, and 10 the gas evolved was found to contain carbon dioxide.

[2] Silver dissolved in the formic acid as the result of the oxidation. This was precipitated by adding 1 cc. of N. HCl. Allowance was made for this in getting the N/5 NaOH required.

[3] A control experiment was tried using 5 cc. N. hydrogen peroxide, 5 cc. of water, and 1 cc. of N. potassium iodide. At the end of the experiment this required 0.2 cc. N/5 NaOH to neutralize it. This correction was introduced into the result of Experiment 10.

[4] In a control experiment with 5 cc. of water, 5 cc. of N. hydrogen peroxide and 1 cc. of 2/5 N. hydriodic acid, for fifteen minutes at 60° C., 0.3 cc. of N/5 NaOH was required to neutralize the acid remaining. This was deducted from the amount of N/5 NaOH required in Experiment 14.

[5] The formic acid dissolved a part of the copper during the experiment.

[6] In Experiment 17, 2 N. formic acid was accidentally used instead of the N. acid.

[7] 1 cc. N. hydrogen peroxide required 19.1 cc. of the solution of potassium permanganate employed in these titrations.

hydrogen peroxide; temperature 21° to 24° C.; time, sixteen hours; 0.25 cc. gas evolved. Required 24.6 cc. N/5 caustic soda, hence 1 per cent oxidation.

II. 0.05 gram platinum, with 5 cc. N. formic acid, and 5 cc. N. hydrogen peroxide; temperature, 24° C.; time, two minutes. 76.6 cc. gas evolved. This was found to contain carbon dioxide. Required 13.70 cc. N/5 caustic soda, and 7 cc. potassium permanganate solution. Therefore, 45.2 per cent oxidation and 92.47 per cent hydrogen peroxide decomposed.

The conclusion would therefore seem to be justified that, in general, any substance that can effect the decomposition of hydrogen peroxide can also accelerate oxidations by means of this substance, and that in proportion as a substance is able to break down the peroxide, so also it is able to accelerate oxidations to a corresponding degree. Freshly burned sugar charcoal, for example, decomposes hydrogen peroxide very slowly. It is also a poor oxygen carrier. On the other hand, certain specimens of bone-black decompose hydrogen peroxide rapidly, and these have been found to be good oxygen carriers also.

It has already been indicated above that, if it could be proved that hydrogen peroxide, on decomposition, yields water and atomic (active) oxygen, a very simple and beautiful explanation would be afforded for most, if not all, of the phenomena of oxidation by means of this substance, and also for the accelerating effect of catalyzers on such oxidations. This important point, however, has not as yet been demonstrated. Indeed, as has been pointed out above, quite a number of objections may be urged against it. It occurred to us, therefore, in this connection, that in neutral potassium oxalate we have a substance on which to test this matter experimentally, inasmuch as it has already been proved by Traube[1] that neutral potassium oxalate is not oxidized by boiling with an excess of hydrogen peroxide, whereas on electrolysis in aqueous solution it is vigorously oxidized at the anode.

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[1] Ber. d. chem. Ges., **26**, 1476 (1893).

In view of this interesting observation, it occurred to us that it would be of some importance to test the conduct of the oxalate towards hydrogen peroxide in the presence of platinum black and liver catalase, as oxygen carriers.

Accordingly, a solution of neutral potassium oxalate was prepared containing 18.4280 grams per liter. Ten cc. of this solution were found to require 19.85 cc. of N/10 potassium permanganate. With this solution the following experiments were tried:

I. 10 cc. of the potassium oxalate solution, with 5 cc. of water and 10 cc. of the 3 per cent hydrogen peroxide,[1] were allowed to stand fifteen minutes at ordinary temperature, at the end of which time the mixture was found to be neutral. The oxalate remaining in the solution was determined in 10 cc. of the solution by precipitating with calcium chloride, filtering, and titrating the calcium oxalate with N/10 potassium permanganate. It required 8.1 cc. N/10 permanganate. Therefore, the whole of it required 20.25 cc. N/10 permanganate.

II. 10 cc. of the solution of potassium oxalate, with 5 cc. of water, 10 cc. of hydrogen peroxide and 0.05 gram platinum black. Time and temperature, the same as in Experiment I. On adding the platinum a vigorous decomposition of the peroxide took place. The oxalate remaining at the end of this experiment was determined as in I., and was found to require 19.25 cc. N/10 permanganate. The solution was found to have an alkalinity at the end equal to 0.25 cc. N/10 caustic soda.

III. 10 cc. solution of potassium oxalate, with 5 cc. 10 per cent extract of hog liver and 10 cc. of hydrogen peroxide. Time and temperature, the same as in Experiment I. On adding the extract of liver a vigorous decomposition of the peroxide occurred. At the conclusion of the experiment the solution was found to be very faintly acid. The oxalate remaining was determined as in Experiments I. and II. It required 20 cc. N/10 permanganate. In this connection it was observed that the liver catalase was not destroyed, or even materially weakened, by standing for some time in contact with the amount of potassium oxalate employed in these experiments.

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[1] The hydrogen peroxide used in these experiments was neutralized with caustic soda before using.

IV. In this experiment the same quantities of substances were employed as in Experiment I., the only difference being that in this experiment the mixture was boiled for five minutes. The solution was then cooled and the amount of oxalate remaining at the end of the experiment was determined as indicated above. 19.6 cc. N/10 permanganate were required.

V. In this experiment the same conditions were observed and the same amount of substances employed as in Experiment IV., except that 0.05 gram of platinum was added to the boiling solution. A very vigorous decomposition of the hydrogen peroxide occurred on adding the platinum. The solution was then filtered, and the oxalate remaining in the clear filtrate was determined in the manner already described. 19.4 cc. N/10 permanganate were required.

It is evident, from the results of these experiments, that platinum black and liver catalase are unable to effect the oxidation of neutral potassium oxalate by hydrogen peroxide. Now bearing in mind the observation of Traube, that neutral potassium oxalate is oxidized by the oxygen liberated at the anode in electrolysis, that is, by active (atomic) oxygen, it would seem from the results reached in the above experiments, that the oxygen liberated from hydrogen peroxide by platinum and catalase is not atomic but molecular oxygen, and that, therefore, it is incorrect to represent the decomposition of the peroxide by the equation

$$H_2O_2 = H_2O + O,$$

even though the decomposition be one of the first order.

State College of Kentucky,
January 15, 1903.

EQUILIBRIUM IN THE SYSTEM COMPOSED OF SODIUM CARBONATE, SODIUM BICARBONATE, CARBON DIOXIDE, AND WATER.

By Herbert N. McCoy.

The conversion of dry sodium bicarbonate into the normal carbonate, water, and carbon dioxide requires but a very moderate degree of heat. Complete decomposition takes place rapidly at 100° to 110°.[1] Gautier found that no loss of weight occurs when the salt is placed in a vacuum at 25°. At 35° an appreciable loss had occurred at the end of four days.

Solutions of sodium bicarbonate are far less stable than the dry salt. Rose[2] observed that a solution of sodium bicarbonate loses carbon dioxide by evaporation and leaves nearly pure normal carbonate. The same change was found to occur, at ordinary temperature, when the solution was allowed to evaporate under such conditions that the carbon dioxide given off could be absorbed by caustic potash. Magnus[3] found that carbon dioxide is removed from a solution of sodium bicarbonate at ordinary temperatures by a stream of hydrogen, and Marchand[4] obtained a similar result by drawing air through a saturated solution of sodium bicarbonate at a temperature of 0°. At 38° Marchand found that about 95 per cent of the bicarbonate was converted into normal carbonate, after drawing a rather large volume of air through the solution, and concluded that the change would be complete after sufficiently prolonged action of the air.

Dibbits[5] has pointed out the errors in the determination of the solubility of bicarbonates arising from a failure, on the part of previous experimenters, to prevent loss of carbon dioxide. In his own work on such determinations the loss of carbon dioxide was reduced to a minimum by working in closed vessels which were nearly filled by the solutions. In connection with this work Dibbits determined roughly the pressure with which carbon dioxide is evolved by saturated solutions of sodium and potassium bicarbonates at several temperatures. He obtained the following results with sodium bicarbonate.

Table I.

Temperature.	Pressure, in mm. of mercury.
15°	120
30°	212
40°	356
50°	563

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[1] Gautier: Ber. d. chem. Ges., 9, 1434 (1876).

[2] Pogg. Ann., 34, 158 (1835).

[3] *Ibid.*, 40, 590 (1837).

[4] J. prakt. Chem., 35, 389 (1845).

[5] *Ibid.*, [2], 10, 417 (1874).

Treadwell and Reuter,[1] in connection with another problem, made a few determinations of the composition of a sodium bicarbonate solution, of decinormal strength, when the partial pressure of the carbon dioxide was varied between 2 and 4 per cent of one atmosphere. They concluded that the bicarbonate lost carbon dioxide at reduced pressures, but made no attempt to study equilibrium conditions.

The consequence of a loss of carbon dioxide by solutions of sodium bicarbonate, in connection with analyses of carbonates and bicarbonates and of gases containing carbon dioxide, have, at times, been understood and taken into account. Thus Lunge[2] takes precautions to prevent loss of carbon dioxide from mixtures of carbonates and bicarbonates previous to and in the course of analysis. Lunge and Zeckendorf,[3] and also Rosenthal,[4] recognize the dissociation of sodium bicarbonate in aqueous solution as the cause of the incomplete absorption of traces of carbon dioxide by solutions of sodium carbonate. On the other hand, the change, during analysis, of sodium bicarbonate into normal carbonate was observed by Cameron[5] without, at the time,[6] the true cause being discovered.

The loss of carbon dioxide by solutions of bicarbonates is the necessary consequence of four things: (1) The weakness of carbonic acid, as an acid; (2) the acid nature of sodium bicarbonate; (3) the ready dissociation of carbonic acid into water and carbon dioxide; (4) the comparatively slight solubility of carbon dioxide in water.

The hydrolytic dissociation of sodium bicarbonate is represented by the equation:

$$NaHCO_3 + H_2O \rightleftarrows NaOH + H_2CO_3.$$

The carbonic acid existing thus in solution will necessitate a certain gaseous pressure of carbon dioxide, the ratio of the concentrations in the two phases being simply the solubility, as Ostwald uses the term. In a system composed of dilute sodium bicarbonate and vapor, the concentration of the carbon dioxide in the vapor must, therefore, be a direct measure of that of the free carbonic acid in the solution. It might seem then, at first thought, that by measuring the concentration of the carbon dioxide in the vapor in equilibrium with a solution of sodium bicarbonate of known strength one would be able to determine the degree of hydrolytic dissociation of the salt.[1] But the equilibrium in the system in question must be more complex than is indicated by the above equation, as the following considerations show: The immediate result of the action of water on the bicarbonate is doubtless the formation of some sodium hydroxide and free carbonic acid. This action would naturally be expected to reach a state of equilibrium by reason of the reverse reaction. However, the bicarbonate is itself an acid and can act upon the free sodium hydroxide, forming water and the normal carbonate, thus:

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[1] Ztschr. anorg. Chem., **17**, 202 (1898).

[2] Ztschr. anal. Chem., **37**, 689 (1898).

[3] *Ibid.*, **36**, 329 (1897).

[4] *Ibid.*, **36**, 333 (1897).

[5] This Journal, **23**, 473 (1900).

[6] The more recent work of Cameron and Briggs (J. Phys. Chem., **5**, 537) is discussed later.

$$NaHCO_3 + NaOH \rightleftarrows Na_2CO_3 + H_2O.$$

This last equation is really that of the hydrolytic dissociation of sodium carbonate. Though carbonic acid is much stronger, as an acid, than sodium bicarbonate, the relatively great concentration of the latter, as compared with the former, makes it necessary to consider the quantitative effect of the action of this acid salt on the sodium hydroxide produced by the primary hydrolysis.

The equilibrium in aqueous solutions of sodium bicarbonate is, therefore, governed by the two reactions just discussed, each of which represents the hydrolytic dissociation of a salt of a weak acid and a strong base. Walker has shown[2] that for dilute solutions the product of the concentrations of base and acid divided by that of the salt is a constant. It is well known that the same relationship governs the hydrolytic dissociation of salts of strong bases and weak acids,[3] it being presupposed that both the salt, and in the latter case, the base, are highly ionized and to practically the same extent.[4]

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[1] See page 450.

[2] Ztschr. phys. Chem., 4, 324 (1889).

[3] Van 't Hoff: Vorlesungen über theoretische und physikalische Chemie, 1, 124 (1901).

[4] Arrhenius: Ztschr. phys. Chem., 5, 17 (1890).

From the reaction

$$\underset{C_1}{NaHCO_3} + H_2O \rightleftarrows \underset{C_3}{NaOH} + \underset{C_4}{H_2CO_3},$$

where C_1, etc., represent concentrations in gram-molecules per liter, we have

$$C_3C_4 = K_1C_1; \qquad (1)$$

and from

$$\underset{C_1}{NaHCO_3} + \underset{C_3}{NaOH} \rightleftarrows H_2O + \underset{C_2}{Na_2CO_3}$$

we have

$$C_1C_3 + K_2C_2; \qquad (2)$$

K_1 and K_2 being the dissociation constants. From (1) and (2)

$$\frac{C_1^2}{C_2C_4} = \frac{K_2}{K_1} = K. \qquad (3)$$

K is the equilibrium constant for the system under consideration.

In a paper entitled "The Solubility of the Alkali-earth Carbonates in Water Containing Carbon Dioxide,"[1] Bodländer has worked out in a different way from that given above, the equation governing the equilibrium in the reaction,

$$2HCO_3' = CO_3'' + H_2O + CO_2,$$

where HCO_3' and CO_3'' refer to ionic concentrations. He gives

$$(HCO_3')^2 = CO_3'' \times CO_2 \times \text{a constant}.$$

This equation and (3) are practically identical for dilute solutions, where one may neglect the factors for ionization. Bodländer applied this equation to the experiments of Schloesing[2] on the solubility of the carbonates of calcium and barium in water containing carbon dioxide, and to those of a similar nature of Engel[3] on magnesium carbonate. Good results were obtained for the equilibrium constant. In the last paragraph of this paper Bodländer shows that the cause of the increased solubility of sodium bicarbonate in water, when shaken with air, is due to loss of carbon dioxide and consequent formation of sodium carbonate. The calculated increase of solubility agrees approximately with the observed value. The discussion regarding the carbonates of sodium is brief and no reference is made to other work on this subject.

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[1] Ztschr. phys. Chem., **35**, 32 (1900).

[2] Compt. rend., **75**, 1552 ; **78**, 70 (1872).

[3] *Ibid.*, **100**, 352, 444 (1885).

In equation (3) C_4 may be expressed in terms of the partial pressure, P, of the carbon dioxide and a constant, k, whose value depends upon the solubility of carbon dioxide in water, thus:

$$C_4 = kP.$$

According to Just,[1] 1 liter of water at 25° dissolves 0.8256 liter of carbon dioxide measured at 25° and 760 mm. The concentration of such a solution is, therefore, 0.0338 normal molecular.

$$C_4 = 0.0338\ P.$$

C_1 and C_2 may readily be expressed in terms of a single variable. Let 1 gram-molecule of sodium bicarbonate be dissolved in the volume, V, of water. Let x represent the number of gram-molecules of sodium bicarbonate after equilibrium has been reached. $1 - x$ is the number of gram-molecules of bicarbonate changed into carbonate, and $\frac{1}{2}(1 - x)$ is the number of gram-molecules of carbonate formed.

As is shown on page 452, the concentration of the hydroxide formed is so minute that it may be left out of consideration in this connection. Its maximum amount did not exceed 0.2 per cent of either x or $1 - x$ for the solutions studied.

$$C_1 = \frac{x}{V}. \qquad C_2 = \frac{\frac{1}{2}(1 - x)}{V}.$$

Therefore

$$\frac{C_1^2}{C_2 C_4} = \frac{2x^2}{0.0338\ PV\ (1 - x)} = K.$$

Calling the concentration of the sodium in gram-atoms per liter C, we have

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[1] Ztschr. physiol. Chem., 37, 342 (1901).

$$C = \frac{1}{V};$$

the equilibrium equation then becomes

$$\frac{2x^2 C}{0.0338\, P\, (1 - x)} = K.$$

The present work was undertaken with the view of testing the correctness of these deductions. After the experiments had been started a paper appeared[1] by Cameron and Briggs under the title: "Equilibrium between Carbonates and Bicarbonates in Aqueous Solution." The authors drew air through aqueous solutions of the bicarbonates of sodium, potassium, and magnesium of various concentrations, and at four different temperatures, and determined by analysis the proportions of carbonate and bicarbonate after equilibrium had been reached. It is rather remarkable that no reference is made, in their paper, to any previous record of loss of carbon dioxide by bicarbonate solutions. Inasmuch as no quantitative application of the law of mass-action to this equilibrium was attempted by Cameron and Briggs, the work here reported was continued.

The experimental problem presented was the determination of the composition of the liquid and vapor phases in equilibrium with one another at constant temperature, for various proportions of the constituents. The temperature chosen was 25°. The method adopted consisted in shaking 200 or 300 cc. of the solution of the mixed carbonates, contained in a closed liter bottle, with air until equilibrium was reached, the whole being kept at constant temperature. A sample of the gas was transferred to another vessel and its percentage of carbon dioxide determined. The composition of the solution was determined by analysis.

A number of the best methods of analyzing carbonate solutions have been critically studied by Küster.[2] The result of this careful piece of work was to show that, of all methods, that of Winkler is most accurate. This method, as applied to solutions containing bicarbonates, consists in adding, in excess, a known volume of standard alkali, free from carbonate, precipitating the carbonate by addition of barium chloride, and finally titrating the excess of alkali with hydrochloric acid, using phenolphthaleïn as indicator.

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[1] J. Phys. Chem., **5**, 537 (1901).

[2] Ztschr. anorg. Chem., **13**, 127 (1897).

This method was tested by means of preliminary analyses, carried out as follows: The necessary amount of barium chloride solution was first brought into an 80 cc. flask, then the measured volume of standard alkali was added, and finally 10 cc. of the carbonate solution was run into this directly from the pipette. When two or three analyses of the same solution were to be made, the flasks were all charged with the barium chloride and standard alkali, and corked. Then the carbonate solution was measured from the pipette into each flask with as little loss of time as possible. After mixing, the flasks were tightly closed with rubber stoppers and allowed to stand a few minutes, after which the excess of alkali was titrated with decinormal hydrochloric acid. The net amount of alkali used (that is, the whole amount added less that neutralized by acid in the final titration) is a measure of the carbon dioxide in excess of that existing as normal carbonate.

In three determinations, using in each 9.90 cc. of a bicarbonate solution, there were required, in each analysis, exactly 10.60 cc. of the standard barium hydroxide solution. In three other determinations, using in each 9.90 cc. of a different bicarbonate solution, there were required 10.42, 10.42, and 10.40 cc., respectively, of barium hydroxide. By working in the manner just described, no carbon dioxide could be lost by the bicarbonate solution in the course of the analysis, and practically none absorbed from the air by the standard alkali.

Carbon dioxide may readily be lost during analysis from solutions rich in bicarbonate, if care be not taken to render them alkaline at once. Low results were invariably obtained when, instead of working in the manner described, the bicarbonate solutions were measured into beakers and allowed to stand, even for four or five minutes, before adding an excess of alkali.

The concordant results given above, together with those of the elaborate work of Küster, are sufficient to show the accuracy of the analytical method used in the determination of the carbon dioxide in the solutions.

In order to calculate the amounts of carbonate and bicarbonate in any solution containing a known amount of carbon dioxide, it is necessary to know the total amount of sodium. This was determined by titration with standard hydrochloric acid, using methyl orange as indicator, and taking for the end reaction the "normal color" produced by the indicator when dissolved in water saturated with carbon dioxide. This method, recommended by Küster,[1] gives excellent results.

For the determination of carbon dioxide in mixtures of this gas with air, the sample was brought into a half-liter separatory-funnel closed by a perforated stopper. An excess of barium hydroxide was run in rapidly from a burette by inserting the tip of the burette in place of the glass plug of the rubber stopper. A solid stopper was then substituted for the perforated one. In doing this a quantity of gas escaped equal in volume to that of the barium hydroxide added. The solution was shaken vigorously with the gas for ten minutes. (Absorption of the carbon dioxide seemed to be complete in from one to two minutes.) The excess of alkali was then determined by titration with standard hydrochloric acid. Phenolphthaleïn was used as indicator.

The transference of the gas from the equilibrium-bottle to the vessel in which it was analyzed required some care. For, since the equilibrium depends on the temperature and pressure, any change in these conditions during the process of separation of the phases is not permissible. The equilibrium-vessel consisted of a liter bottle. It was fitted with a rubber stopper, through one hole of which passed the stem of a 100 cc. separatory-funnel, through the other hole a bent tube with glass stop-cock. The stem of the separatory-funnel nearly reached the bottom of the bottle. The carbonate solution, to the amount of 200 to 300 cc., was placed in the bottle and the stopper, carrying the separatory-funnel and tube, was inserted and carefully wired. The bottles thus charged were placed in a large thermostat, the temperature of which was kept constant at 25° (±0.01°). While in the thermostat, the bottles were constantly shaken by means of a device giving a rather rapid rocking motion. The total pressure of the gas phase was made nearly equal to the normal atmospheric pressure by opening the stop-cock of the bent tube occasionally during the first hour or two after starting. The attainment of equilibrium under these conditions required two or three days, as shown by special experiments made to determine this point. In the recorded experiments the time allowed was five days or more. Immediately before removing a bottle from the thermostat, preparatory to the analysis of its contents, the gas pressure was determined by measuring, with a simple manometer, the excess or deficiency of pressure with respect to the existing barometric pressure. This was readily done by attaching the manometer to the bent tube having the stop-cock. The transference, for analysis, of the larger part of the gas to a large separatory-funnel of known volume was accomplished at constant (atmospheric) pressure in the following manner: The end of the bent tube of the equilibrium apparatus was connected by a short rubber tube with one tube of a three-way stop-cock. A second tube of the three-way cock was connected by a rubber tube with a perforated rubber stopper which fitted the large funnel, into which the gas was to be transferred. The third tube of the three-way cock was attached to a thin-walled rubber bulb of about 50 cc. capacity. To transfer the gas, the stem of the small separatory-funnel of the equilibrium apparatus was filled with the carbonate solution by applying suction at the mouth of the funnel and opening its stop-cock, the other cock of the apparatus being meanwhile kept closed. The small separatory-funnel was then filled with pure dry mercury, and the rubber bulb and the tubes leading to the large funnel were rinsed with the gas which was displaced by allowing the mercury to run into the equilibrium-bottle. The large separatory-funnel was completely filled with mercury and connected with the delivery-tube from the three-way cock. It was supported above the equilibrium-bottle in such a way that the mercury could flow from the former into the smaller separatory-funnel. By opening the stop-cocks of the two separatory-funnels partially and the other two cocks completely, the gas was readily transferred. The rubber bulb, being in direct communication with the two vessels, indicated, by its dilations or contractions, the adjustments necessary to secure an equal flow of mercury through the two stop-cocks. It served, at the same time, to keep the pressure equal to the barometric pressure. Constant temperature, during transference, was secured by placing the bottle in a vessel of water kept at 25° (±1°).

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[1] *Loc. cit.*

The main series of experiments was made with solutions of bicarbonate and carbonate in various proportions, and of decinormal strength with respect to sodium. Such solutions, of approximately the desired composition, were made from separate solutions of bicarbonate and carbonate, each having the same concentration of sodium.

The method of calculating the equilibrium constant from the analytical data can doubtless best be shown by an example (Experiment 1, Table II.).

Analysis of the Gas.

Volume of the separatory-funnel	550 cc.
Barometric pressure	743 mm.
Excess pressure in equilibrium-bottle	2 "
Total " " "	745 "
Temperature of the gas in the separatory-funnel immediately before analysis	28.2°

Added 10 cc. dilute barium hydroxide (= 2.15 cc. N/10 hydrochloric acid). Ten cc. of gas escaped. After absorption of the carbon dioxide, the excess of alkali required, using phenolphthaleïn, 1.44 cc. of acid.[1]

$2.15 - 1.44 = 0.71$ cc. N/10 acid.

1 cc. of N/10 acid = 1.12 cc. of carbon dioxide gas at 0° and 760 mm.

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[1] **In titrations requiring small volumes of solutions (as in this case) a special gravimetric burette, holding about 4 cc., was employed, and the amounts of solution used were determined by weighing. Much greater accuracy was thereby secured.**

$0.71 \times 1.12 = 0.79$ cc = the volume of the carbon dioxide at 0° and 760 mm.

$\frac{0.79 \times (273 + 28) \times 760}{540 \times 273 \times 743}$ = the fraction of the total pressure exerted by the carbon dioxide.

The total pressure of the vapor phase is $\frac{745}{760}$ of one atmosphere.

Therefore, the partial pressure of the carbon dioxide, P, is

$$\frac{0.79 \times 301 \times 745}{540 \times 273 \times 743} = 0.00161 \text{ atmosphere.}$$

From which we get:

$$k\text{P} = 0.0338 \times 0.00161 = \text{C}_4.$$

Analysis of the Carbonate Solution.

The exact concentration of the carbonate solution was found from the titration in presence of methyl orange:

9.94 cc. of carbonate solution required 9.93 cc. of N/10 acid.

Therefore the solution was 0.0999 normal with respect to sodium.

9.94 cc. of the carbonate solution was run into 7.49 cc. N/10 barium hydroxide and 2 cc. of approximately N/2 barium chloride. The excess of alkali required 0.70 cc. N/10 hydrochloric acid. The difference, 6.79 cc., was, therefore, the amount of barium hydroxide required to neutralize all of the carbon dioxide in the solution in excess of that needed to form the normal carbonate with the sodium. The larger part of this was united to form bicarbonate, but a small amount was present as free carbonic acid. The concentration of the free carbonic acid, considered as monobasic, has just been found to be 0.00161×0.0338 normal. In neutralizing barium hydroxide it is dibasic. The volume of N/10 barium hydroxide required to neutralize 10 cc. of carbonic acid of this strength is, therefore:

$10 \times 10 \times 2 \times 0.0161 \times 0.0338$ cc. = 0.01 cc., the correction for the free carbonic acid in the solution.

$6.79 - 0.01 = 6.78$ cc., the amount of barium hydroxide required for the bicarbonate alone.

$$6.78/9.93 = 0.683.$$

68.3 per cent of the sodium was in the form of bicarbonate. The duplicate analysis gave 68.1 per cent. Mean, 68.2 per cent. Therefore,

$$x = 0.682. \quad 1 - x = 0.318. \quad P = 0.00161, \quad k = 0.0338.$$

Substituting these values in the formula

$$\frac{2x^2\,C}{kP(1-x)} = K,$$

we get

$$\frac{2 \times 0.682^2 \times 0.0999}{0.0338 \times 0.00161 \times 0.318} = 5320 = K.$$

The following table shows the results obtained with solutions decinormal with respect to sodium. The fourth column contains the apparent percentages, A, of bicarbonate. These values, corrected in the manner described for the free carbonic acid in the solution, give the real percentages of bicarbonate as contained in the fifth column :

Table II.

	Barometric pressure.	Excess pressure.	A.	100x.	100P.	$K \times 10^{-2}$.
1	743	2	68.3	68.2	0.161	53.2
2	740	2	69.1	69.0	0.159	57.0
3	745	2	76.2	76.0	0.259	54.6
4	742	3	77.7	77.5	0.294	53.6
5	743	10	78.3	78.1	0.322	51.0
6	743	3	82.1	81.8	0.404	53.6
7	745	0	96.6	95.1	2.23	49.0
8	740	24	103.6	98.5	7.49	51.0
					Mean,	52.9

The above results represent all experiments carried to completion on solutions of this concentration, after the method, as described, had been fully worked out. An inspection of the formula for the equilibrium constant will show that, for certain proportions of the reacting substances, very small errors in the analyses will cause large errors in the value of K. This is obviously the case, on the one hand, when the percentage of bicarbonate becomes so high that $1-x$ approaches zero and, on the other hand, when P becomes very small on account of the large proportion of carbonate. The most favorable condition for the accurate determination of K is found when x lies between 75 and 85 per cent. In accordance with this it may be seen, from the table, that the smallest variations in the value of K are found between these limits. The average value of K, as given by these four determinations, is 53.2×10^2. This is the most probable value of the constant.

Walker[1] has calculated, from the ionization constant of carbonic acid, the theoretical value of the hydrolytic dissociation of sodium bicarbonate. This was done by means of the well-known formula of Arrhenius[2] which here becomes

$$K_1 = \frac{K_{H_2O}}{K_{H_2CO_3}}.$$

The closely agreeing results of the determinations of the magnitude of the dissociation constant of water by Ostwald,[3] Wys,[4] Arrhenius,[5] and Kohlrausch and Heydweiller,[6] give as an average value,[7]

$$K_{H_2O} = 1.2 \times 10^{-14}.$$

The constant of carbonic acid, as measured by the conductivity method by Walker and Cormack,[8] gave the value,

$$K_{H_2CO_3} = 3.04 \times 10^{-7},$$

the concentration of the carbonic acid being expressed in gram-molecules per liter.

Therefore,

$$K_1 = \frac{1.2 \times 10^{-14}}{3.04 \times 10^{-7}} = 3.95 \times 10^{-8}.$$

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[1] Ztschr. phys. Chem., **32**, 137 (1900).
[2] *Ibid.*, **5**, 17 (1890).
[3] *Ibid.*, **11**, 521 (1893).
[4] *Ibid.*, **11**, 492 (1893).
[5] *Ibid.*, **11**, 827 (1893).
[6] *Ibid.*, **14**, 317 (1894).
[7] Van 't Hoff: Vorlesungen, **1**, 127.
[8] J. Chem. Soc. (London), **77**, 5 (1900).

But

$$K_1 = \frac{C_{NaOH} \times C_{H_2CO_3}}{C_{NaHCO_3}}. \qquad \text{(Equation 1.)}$$

From these relationships Walker obtained the hydrolytic dissociation of a decinormal solution of sodium bicarbonate, 0.06 per cent. This value is really fictitious, for the reason shown on page 440. This is clearly seen when we consider that for 0.06 per cent hydrolysis the concentration of the carbonic acid in the decinormal bicarbonate solution would be 0.00006 normal molecular. The concentration of carbonic acid in water, saturated at atmospheric pressure at 25°, is 0.0338 normal molecular. Therefore, the pressure of a 0.00006 normal solution is only 0.0018 atmosphere. From Table II. it is seen that a decinormal solution containing but 96 per cent of bicarbonate gives a partial pressure of more than twelve times this amount.

The actual concentrations of the free carbonic acid and of the sodium hydroxide in a decinormal solution, made from solid bicarbonate and water in such a way that no carbon dioxide is allowed to escape, may readily be calculated. Since the amount of free hydroxide in such a solution is extremely minute, as is shown below, we may represent the net result of the hydrolytic dissociations thus:

$$\underset{C_1}{2NaHCO_3} \rightarrow \underset{C_2}{Na_2CO_3} + \underset{C_4}{H_2CO_3}.$$

If

$$\frac{x}{V} = C_1. \qquad \frac{1-x}{2V} = C_2 = C_4.$$

$$K = \frac{C_1^2}{C_2C_4} = \frac{4x^2}{(1-x)^2} = 5290.$$

From which

$$x = 0.9732 \qquad \text{and} \qquad 1 - x = 0.0268.$$

In such a solution 2.68 per cent of the bicarbonate would have been converted into carbonate and free carbonic acid. It will be observed, further, that the equation involving x does not contain V. The value of x is, therefore, independent of the dilution. For a decinormal solution

$$C_4 = \frac{1 - x}{2 \times 10} = 0.00134;$$

$$P = \frac{0.00134}{0.0338} = 0.0396;$$

from which it follows that a decinormal solution of sodium bicarbonate will evolve carbon dioxide if the partial pressure of the gas is less than 4 per cent of 1 atmosphere. Now for the bicarbonate solution we have

$$K_1 = \frac{C_{NaOH} \times C_{H_2CO_3}}{C_{NaHCO_3}} = 3.95 \times 10^{-8};$$

$$C_{H_2CO_3} = C_4 = 0.00134;$$

$$C_{NaHCO_3} = C_1 = 0.097.$$

Therefore,

$$C_{NaOH} = 2.9 \times 10^{-6}.$$

This value, which is but 1/20 of that calculated by Walker,[1] represents the true degree of alkalinity of a freshly prepared decinormal solution of sodium bicarbonate. Solutions consisting of mixtures of bicarbonate and carbonate contain, of course, more free sodium hydroxide. Thus the concentration of sodium hydroxide in solution 1, Table II., is readily calculated to be 5.0×10^{-5}.

According to equation 3, page 441, we have

$$K_2 = KK_1,$$

where K_1 is the constant for the hydrolytic dissociation of sodium bicarbonate and K_2 that for the carbonate,

$$K = 5290; \qquad K_1 = 3.95 \times 10^{-8};$$

from which

$$K_2 = 2.08 \times 10^{-4}.$$

The percentage of hydrolytic dissociation of sodium carbonate may be calculated from the value of this constant by means of the formula,

$$K_2 = \frac{m^2}{(1 - m)V} = 2.08 \times 10^{-4},$$

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[1] Ztschr. phys. Chem., 32, 137 (1900).

where m is the fraction of the carbonate existing as hydroxide and bicarbonate. For a solution containing 0.5 gram-molecule in 10 liters, $m = 0.062$. That is, in a solution decinormal with respect to sodium, 6.2 per cent of the sodium carbonate is split by the action of water into sodium hydroxide and sodium bicarbonate. The concentration of the hydroxide in such a solution is 0.0031 normal.

The hydrolytic dissociation of sodium carbonate has been studied by Shields.[1] The amount of free base was calculated from the velocity of saponification of ethyl acetate at 24°.2. Shields gives as the value of the constant for a 0.0477 gram-molecular solution[2]

$$(100)K_2 = 0.02382.$$

That is,

$$K_2 = 2.38 \times 10^{-4},$$

while I find, at 25°,

$$K_2 = 2.08 \times 10^{-4}.$$

The agreement seems to be very good. But it appears, upon critical inspection of the method of calculation, that Shields has assumed that each molecule of carbonate, when hydrolyzed, gives 2 molecules of hydroxide, thus:

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3.$$

As this is not the case to any appreciable extent, it would seem that the method of calculation is not correct. The results of these experiments of Shields have been recalculated for the 0.0477 molecular solution on the basis of a dissociation into 1 molecule each of hydroxide and bicarbonate. The average value of K_2 thus found is 1.04×10^{-4}, from which the percentage of carbonate molecules changed to hydroxide and bicarbonate is calculated to be 4.6. My own experiments lead to the value 6.2 per cent for a 0.05 gram-molecular solution. Shields calculates that 4.87 per cent of the carbonate molecules each give two of hydroxide.

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[1] Ztschr. phys. Chem., 12, 167 (1893).

[2] Shields calls this K and not 100K, as I have written it and as it really should be. See van Laar: *Ibid.*, 12, 745 (1893).

Walker and Cormack[1] have shown that the ionization of carbonic acid is chiefly into H and HCO_3. The constant for the second H ion is fixed by the relation,

$$C_H \times C_{CO_3} = K_2 C_{HCO_3}.$$

The value of K_2 has been calculated by Bodländer[2] from the work of Shields. Bodländer finds

$$K_2 = 1.295 \times 10^{-11}.$$

K_2 may be calculated from any experiment recorded in Table II. Experiment 6 may be chosen, as it probably represents the most favorable composition for the accurate analytical determination of all the factors, x, $1 - x$, and P.

$$x = 0.818. \qquad 1 - x = 0.182. \qquad P = 0.00404.$$

Since practically all of the HCO_3 ions come from the sodium bicarbonate, we have

$$C_{HCO_3} = 0.1 \times 0.818 \times \alpha,$$

where α is the degree of ionization of the bicarbonate. By an extrapolation of Walker and Cormack's figures the degree of ionization of 0.1 molecular sodium bicarbonate is calculated to be 0.81. Therefore,

$$C_{HCO_3} = 0.0818 \times 0.81 = 6.63 \times 10^{-2}.$$

Similarly the concentration of CO_3 depends upon the concentration of the sodium carbonate and on its degree of ionization. If we consider the ionization of the carbonate to be the same as that of sodium sulphate,[3] at equal concentration, we have for a 0.05 molecular solution 0.70. Therefore,

$$C_{CO_3} = 0.5 \times 0.0182 \times 0.70 = 6.37 \times 10^{-3}.$$

Now,

$$C_H \times C_{HCO_3} = 3.04 \times 10^{-7} \times C_{H_2CO_3};$$

$$C_{H_2CO_3} = 0.00404 \times 0.0338 = 1.37 \times 10^{-4};$$

$$C_H = \frac{3.04 \times 1.37 \times 10^{-11}}{6.63 \times 10^{-2}} = 6.28 \times 10^{-10}.$$

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[1] J. Chem. Soc. (London). **77**, 5 (1900).

[2] *Loc. cit.*

[3] Kohlrausch: Wied. Ann., **26**, 161 (1885).

Therefore,

$$K_3 = \frac{6.28 \times 6.37 \times 10^{-13}}{6.63 \times 10^{-2}} = 6.04 \times 10^{-11}.$$

The considerable difference between this result and that of Bodländer is in large measure due to Shields' error in calculating the hydrolysis of sodium carbonate. A comparison of K_3 with the ionization constant for the first H ion of carbonic acid shows that the latter is 5040 times as large as the former. Since the degrees of ionization, at the same concentration, of two weak acids are proportional to the square roots of their ionization constants, the degree of ionization of the first H ion of carbonic acid is $\sqrt{5040}$, or 71 times as great as that of the second H ion. The ionization constants of several very weak acids are all greater than K_3, as the following figures of Walker and Cormack show:

		Constant $\times 10^{-10}$.
	Carbonic acid (first H ion)	3040.0
	Hydrogen sulphide	570.0
	Boric acid	17.0
	Prussic acid	13.0
	Phenol	1.3
I find:	Carbonic acid (second H ion) = K_3	0.6

In very dilute solutions sodium bicarbonate is highly ionized into Na and HCO_3. The ionization, K_4, of sodium bicarbonate as an acid is, therefore, practically equal to K_3 for such solutions. Sodium bicarbonate may also split into H and $NaCO_3$ ions, and it is probable that the constant of this ionization is about the same as K_3. If this is the case, K_4 in solutions not dilute is also nearly equal to K_3. The constant, K_4, may also be obtained, at least approximately, by dividing the constant for the dissociation of water by K_2, the constant for the hydrolytic dissociation of sodium carbonate.

$$K_4 = \frac{K_{H_2O}}{K_2} = \frac{1.2 \times 10^{-14}}{2.08 \times 10^{-4}} = 0.58 \times 10^{-10},$$

a quantity which does not differ greatly from the value of K_3 found above.

The formula for the equilibrium of the system composed of carbon dioxide and the aqueous solution of the carbonates of sodium, has been derived upon the supposition that the solution was dilute. It is not to be expected, therefore, that the value of K would be the same for concentrated solutions. Deviations from the simple relationships, which hold for dilute solutions, may be due to three causes: (1) The partial failure of the law of mass action; (2) the change in the ratio of the degrees of ionization, as salts, of the two carbonates; (3) a smaller solubility of carbon dioxide in the stronger solutions than in the dilute solutions, where the solubility has been assumed to be the same as in pure water. Equilibrium experiments with 0.3 normal (Table III.) and with normal solutions (Table IV.) actually gave lower values for K than were found for decinormal solutions, but there is good agreement between various determinations at the same concentration. The following tables show the results obtained:

Table III.

	Barometric pressure.	Excess pressure.	A.	$100x$.	$100P$.	$K \times 10^{-2}$.
1	747	0	58.0	57.9	0.319	44.6
2	748	0	68.0	67.9	0.583	43.8
3	745	0	77.1	76.9	1.044	43.6
4	740	3	85.6	85.2	1.07	44.4
5	740	3	89.4	88.8	2.76	45.4
6	743	2	93.6	92.6	4.51	45.8
					Mean,	44.6

Table IV.

	Barometric pressure.	Excess pressure.	A.	$100x$.	$100P$.	$K \times 10^{-2}$.
1	744	0	76.1	75.8	4.36	32.4
2	737	6	81.4	81.0	6.24	32.8
3	742	2	86.7	86.0	10.21	30.6
4	743	1	91.3	90.2	16.82	29.2
					Mean,	31.2

Equilibrium in Carbonate-bicarbonate Solutions in Contact with Natural Air.

The determination of the amount of carbon dioxide in the air has been the subject of a very large number of extended researches. In a recent paper[1] Letts and Blake have given the results of their own very careful experiments, made at Belfast, together with a tabulated summary of several thousand analyses, made by many observers, in various parts of the world. This summary clearly shows that the percentage of carbon dioxide in air (collected out of doors) is by no means constant. But, if analyses of air from the central portions of crowded cities be excluded, all except a small portion of the results fall between the limits of 2.5 and 3.5 parts by volume of carbon dioxide in 10,000 of dry air. The average value is probably not far from 3 parts in 10,000.

Taking the amount of carbon dioxide as fixed at this value, we may calculate the theoretical composition of carbonate-bicarbonate solutions when in equilibrium with ordinary air, at a temperature of 25°. In the formula

$$\frac{2x^2\,\mathrm{C}}{k\mathrm{P}(1-x)} = \mathrm{K}.$$

P, the partial pressure of the carbon dioxide, is equal to

$$\frac{0.0003\mathrm{H}}{760},$$

where H is the barometric pressure (corrected for aqueous tension) at the time of the experiment. Transposing, we have

$$\frac{x^2}{1-x} = \frac{\mathrm{K} \times \mathrm{H} \times 0.0338 \times 0.0003}{2 \times 760 \times \mathrm{C}}. \qquad (4)$$

In the work of Cameron and Briggs, which has been previously mentioned, one series of experiments on the carbonates of sodium was carried out at 25°. The theoretical results, as indicated by the above formula, have been calculated and compared with the values obtained by these chemists. In making the calculation, H, the corrected barometric pressure, has been assumed equal to 730 mm. The value of K for dilute solutions is practically 53×10^{-2}. The values of K used in calculating the theoretical values of x, for the more concentrated solutions, were obtained by interpolation from the average values of K as found in Tables III. and IV.

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[1] Proc. Roy. Soc. (Dublin), (1900), pp. 107-279.

The comparison of Cameron and Briggs's results with the theoretical values is shown in the following table :

Table V.

Concentration of sodium in gram-atoms per liter.	Value of $K \times 10^{-2}$, used.	Percentage, x, of sodium existing as bicarbonate.	
		Found by C. and B.	Calculated.
0.0044	53	91.3	87
0.0143	53	80.0	72
0.0562	53	62.7	49
0.2248	48	40.7	28
0.8847	33	36.0	13

The differences between the calculated results and those actually found by Cameron and Briggs were so great, especially for the more concentrated solutions, that I was led to make a few experiments of the same nature.

The results of a preliminary experiment may serve to show in a roughly quantitative way the rate of change of composition of an approximately decinormal solution of sodium bicarbonate when a stream of air (taken from out of doors) is drawn through it at the ordinary temperature of the laboratory.

Table VI.

Time in hours.	Percentage of sodium existing as bicarbonate.
0	95
0.25	88
0.67	80
1.17	76
2.00	75
26.0	45
32.0	44
48.0	43
72.0	40
144.0	40

A state of equilibrium is, therefore, reached after about three days.

In a second similar experiment, air was drawn through a solution of sodium carbonate having the same concentration of sodium as the preceding bicarbonate solution. The result was as follows :

Table VII.

Time in hours.	Percentage of sodium existing as bicarbonate.
0	0.3
5.5	5.0
17.0	17.0
24.0	26.0
70.0	40.0

The same state of equilibrium is reached, of course, whether one starts with a carbonate or a bicarbonate solution.

In the following experiments about 200 cc. of the bicarbonate solution were placed in a large Drechsel wash-bottle, which was immersed in a thermostat kept at 25° (±0.01°). The bottle containing the bicarbonate solution was connected on the one side with an aspirating pump and on the other with a wash-bottle containing pure water. Pure air (from out of doors) was supplied by a tube connected with the wash-bottle.

The pressure in the bottle containing the bicarbonate solution was measured by means of a manometer. It was always 8 to 10 mm. (of mercury) less than the atmospheric pressure. The corrected pressure, as given in Tables VIII., IX., and X., is the barometric pressure, corrected for aqueous tension and for the diminution just mentioned.

The following results were obtained in this way, starting with a decinormal solution of sodium bicarbonate.

Table VIII.

Time in days.	Concentration of sodium in gram-atoms per liter.	Corrected pressure.	Percentage of sodium existing as bicarbonate.	
			Found.	Calculated.
0	0.100		95.0	$(K = 53 \times 10_2)$
2			44.1	
3	0.101	710	40.6	39.0
3.2	0.101	713	40.8	39.0

The figures in the last column were obtained by means of Equation 4, page 457, K being taken as 53×10^2. The fact that the solution slowly became slightly more concentrated shows that the air entering the solution was not completely saturated with water vapor.

The results with more concentrated solutions are given in Tables IX. and X.

Table IX.

Time in days.	Concentration of sodium in gram-atoms per liter.	Corrected pressure.	Percentage of sodium existing as bicarbonate. Found.	Percentage of sodium existing as bicarbonate. Calculated.
		(First series.)		
0	0.300		33.0	(K = 45 × 10^3)
1			26.2	
2			24.8	
3	0.312	710	23.9	22.9
		(Second series.)		
0	0.300		22.7	
1	0.306	711	23.1	23.2
2	0.314	714	22.5	22.9

Table X.

Time in days.	Concentration of sodium in gram-atoms per liter.	Corrected pressure.	Percentage of sodium existing as bicarbonate. Found.	Percentage of sodium existing as bicarbonate. Calculated.
0	1.00		13.8	(K = 31 × 10^3)
2	1.03	710	12.2	11.3
3	0.98[1]	714	12.9	11.5
5	0.98	715	12.9	11.5

In the second series of experiments, Table IX., the solution at the start contained a smaller amount of bicarbonate than at the end of one day. This indicates that an absorption of carbon dioxide from the air must have occurred.

A variation in the amount of carbon dioxide in the air necessarily causes a variation in the percentage of bicarbonate in a solution of given concentration. Calculation shows that an increase of 10 per cent of the total carbon dioxide in the air would cause an increase, in a decinormal solution, of only 1.4 per cent of the sodium existing as bicarbonate. In Table VIII., taking the amount of carbon dioxide in the air as 3 parts in 10,000, the percentage of bicarbonate was calculated to be 39.0. For 3.3 parts of carbon dioxide in 10,000 of air the amount would, therefore, be 40.4 per cent. The increase in bicarbonate, for a 10 per cent increase of carbon dioxide, would be 0.9 per cent for a 0.3 normal solution, and for a normal solution but 0.5 per cent.

The ordinary variations in the carbon dioxide content of air rarely exceed ±10 per cent from the assumed value, 3 parts in 10,000 (except in certain localities). Such variations would consequently affect but slightly the state of equilibrium of solutions in contact with the air. In accordance with this it is seen that the agreement between the observed values and those calculated upon the basis of the average concentration of carbon dioxide in the air is very good; and, further, that the small existing differences are no greater than may be accounted for by changes in the amount of atmospheric carbon dioxide.[1]

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[1] The solution was slightly diluted at the end of the second day.

These experiments are, therefore, in complete accord with those of the main series. This being the case, it is difficult to understand the cause of the widely different results obtained by Cameron and Briggs. A possible source of error may be suggested. The authors do not state whether the air used was drawn from out-of-doors or was simply indoor air. In the latter case the amount of carbon dioxide may have been very much higher than in normal air. This would lead to a displacement of the equilibrium in the direction found.

Summary.

1. It has been shown experimentally that the equilibrium in the system composed of sodium carbonate, sodium bicarbonate, carbon dioxide, and water is governed, at constant temperature, by the formula

$$\frac{2x^2C}{kP(1-x)} = K,$$

in which the symbols have the following significance: x is the fraction of sodium in the form of bicarbonate; $1-x$ is the fraction in the form of carbonate; C is the concentration of the sodium in gram-atoms per liter; k is the solubility coefficient of carbon dioxide in water at the equilibrium temperature; and P is the partial pressure of the carbon dioxide. For dilute solutions $K = 53 \times 10^2$.

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[1] As has been mentioned, analyses seem to show that the percentage of carbon dioxide in the air of the crowded portions of large cities is considerably higher than normal. The laboratory of the University of Chicago, where the experiments here described were made, is 6 or 7 miles distant from the central crowded parts of the city, and but a mile from Lake Michigan. In consequence the air used was probably of about normal composition.

2. The degree of hydrolytic dissociation of sodium bicarbonate, as calculated from the ionization constant of carbonic acid, is rendered fictitious by the fact that the bicarbonate is itself a weak acid. The acid carbonate reacts with the free hydroxide produced by the primary hydrolysis, and, on account of its relatively great concentration as compared with that of the free carbonic acid, greatly displaces the equilibrium that would be expected to result from the first action of water on the bicarbonate. For a decinormal solution, the free hydroxide is thereby reduced to about 1/20 of the amount calculated by Walker.

3. The degree of hydrolytic dissociation of sodium carbonate was calculated from the equilibrium experiments. In a solution containing 0.5 gram-molecule of sodium carbonate in 10 liters, 6.2 per cent of the carbonate exists as hydroxide and bicarbonate.

4. The ionization constant of sodium bicarbonate, as an acid, is nearly equal to the constant of the second H ion of carbonic acid. The latter constant is equal to 6.0×10^{-11}, which is but 1/5040 as great as that of the first H ion of carbonic acid.

5. It has long been known that bicarbonate solutions lose carbon dioxide in contact with the air, giving a mixture of carbonate and bicarbonate. The state of equilibrium reached depends on the concentration of the solution, and may be calculated by means of the equilibrium formula, by considering the amount of carbon dioxide in the air as known.

6. The formula given above will hold equally well for solutions of the carbonates of any highly ionized monacid bases. It is probable that it may also be applied to salts of such acids as hydrogen sulphide and sulphurous acid.

Work is being continued along these lines in this laboratory by Mr. H. G. Knight.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO,
December, 1902.

THE EXISTENCE OF HYDROGEN TETROXIDE.

By A. M. Clover.

Hydrogen dioxide, in aqueous solution, behaves as a weak acid. Hanriot[1] and Wolffenstein[2] have proved that a solution of the pure substance reddens litmus. Schönbein,[3] in 1859, noted that hydrogen dioxide could be extracted from an ethereal solution to a much greater extent by a solution of alkali than by pure water. This fact makes it quite probable that hydrogen dioxide enters into chemical union with the alkali.

Calvert[4] has recently studied the condition of hydrogen dioxide in alkaline solution, and in several ways has succeeded in proving that this substance neutralizes alkalies by entering into chemical union with them.

The fact is well known that solutions of the hydroxides of the alkaline-earth metals are precipitated by hydrogen dioxide with the formation of hydrated peroxides of the type $BaO_2.8H_2O$. On the other hand, these substances are dissolved by acids with the liberation of the corresponding amount of hydrogen dioxide. They are therefore to be looked upon as the salts of hydrogen dioxide.

Sodium dioxide,[5] Na_2O_2, is formed when sodium is oxidized in air. The hydrated compound, $Na_2O_2.8H_2O$,[6] separates in the crystalline state, on concentrating a solution of hydrogen dioxide containing the calculated amount of sodium hydroxide. Both of these last-named compounds dissolve in dilute acids with the liberation of the corresponding amount of hydrogen dioxide, and are also to be considered as the salts of this substance. Compounds of potassium[7] and lithium[8] similar to those already mentioned have been studied.

When potassium or rubidium is oxidized by means of air or oxygen, the compounds formed have a percentage composition represented by the formulas KO_2 and RbO_2. Nothing is known concerning the molecular weight of these substances and it is possible that their molecules are represented by the formulas K_2O_4 and Rb_2O_4, just as the peroxide of sodium is ordinarily represented by the formula Na_2O_2, on account of its relation to hydrogen dioxide, whose formula, H_2O_2, has been demonstrated by molecular weight determinations.[1] In this light the peroxides of potassium and rubidium are to be considered as derivatives of the hypothetical tetroxide of hydrogen, H_2O_4.

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[1] Compt. rend., **100**, 172 (1885).

[2] Ber. d. chem. Ges., **27**, 3311.

[3] J. prakt. Chem., [1], **78**, 92.

[4] Ztschr. phys. Chem., **38**, 513.

[5] Harcourt: J. Chem. Soc. (Qu. J.), **14**, 267.

[6] Schöne: Ann. Chem. (Liebig), **193**, 241.

[7] Erdmann and Köthner: *Ibid.*, **294**, 55.

[8] *Loc. cit.*

This view has led Bach[2] to examine the solution obtained by dissolving potassium tetroxide in dilute acid, for the presence of some oxide of hydrogen other than the dioxide. The results of his experiments have led him to conclude that the solution mentioned contains a considerable amount of a higher peroxide which he assumes to be hydrogen tetroxide, H_2O_4.

Wishing to further examine the properties of so interesting a substance, I have attempted to prepare it according to the method of Bach. However, the solution which I have obtained has behaved in all respects as a solution of hydrogen dioxide, and I have not been able, in any way, to detect the presence of any other substance. I have been led, therefore, to repeat the work of Bach with much care, and am forced to conclude that his experimental work is in error, and that there is no evidence whatever of the existence of hydrogen tetroxide.

In examining the solution supposed to contain higher oxides of hydrogen, Bach has made use of the well-known reaction between hydrogen dioxide and potassium permanganate, which takes place according to the following equation:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

The reaction takes place quantitatively, and the amount of hydrogen dioxide in a solution may be estimated by noting the amount of permanganate used or the amount of oxygen evolved.

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[1] Orndorff and White: Ztschr. phys. Chem., **12**, 63.

[2] Ber. d. chem. Ges., **33**, 1506, 3111.

On treating the solution in question with permanganate, Bach has found that the amount of oxygen evolved is in large excess of the theoretical quantity. In one series of experiments the excess amounted to an average of 25 per cent. In another the average excess was 34 per cent. The calculated amount of oxygen was based upon the amount of permanganate used. Since the solution in question could contain nothing but oxides of hydrogen, together with the potassium sulphate formed in the neutralization, Bach seems perfectly justified in drawing the conclusions which he does.

The work of Bach has been previously criticized by Armstrong,[1] who, without submitting experimental evidence, has offered to explain Bach's results by assuming the formation of Caro's acid by the interaction of hydrogen dioxide with the free sulphuric acid present in the solution. This criticism is unjustified, however, in view of Bach's own work, and also in view of the experiments given below with pure hydrogen dioxide. Furthermore, it will be seen later that Bach's results are probably to be attributed to the use of insufficient acid rather than too much.

A few experiments are here given to show what influence the amount of acid used has on the reaction between hydrogen dioxide and permanganate.

I. 5 cc. of a solution of pure hydrogen dioxide[2] were added to a large excess of dilute sulphuric acid (normal) and titrated with N/10 permanganate.

	Required. cc.
1	12.8
2	12.8

II. 5 cc. of the same solution were added to a solution of potassium iodide in dilute sulphuric acid and the iodine liberated was estimated by means of N/10 thiosulphate.

	Required. cc.
1	12.7
2	12.75

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[1] Proc. Chem. Soc., 16, 134.

[2] Jones, Barnes, and Hyde: This JOURNAL, 27, 22.

III. 5 cc. of the same solution were then added to 7.8 cc. N/10 sulphuric acid (calculated amount 7.7 cc.) and titrated with N/10 permanganate.

	Required. cc.
1	12.8
2	12.7

To obtain these results, however, it was necessary to add the permanganate very slowly toward the last, otherwise a considerable quantity of manganese dioxide was precipitated which redissolved very slowly. The results then obtained were low.

IV. 5 cc. of the same solution were added to 3.9 cc. N/10 sulphuric acid (0.5 calculated amount). After the addition of 6.6 cc. N/10 permanganate, a permanent precipitate of manganese dioxide appeared, and the solution, after standing for a few minutes, had lost practically all of the remaining hydrogen dioxide, owing to the catalytic action of the precipitate.

It will be seen from these experiments that the reaction between hydrogen dioxide and permanganate does not take place according to the equation given, unless the required amount of acid be present, and that a large excess of acid has no influence upon the reaction. The reliability of the reaction, either with the minimum quantity or with excess of acid, is shown by the estimation by means of potassium iodide and thiosulphate. I have also made certain that the presence of sodium or potassium sulphates has no influence on the reaction in question, as these substances are present in the solutions to be examined later.

The oxygen evolved by the action of permanganate upon a solution of hydrogen dioxide was also measured, in order to test the reliability of the results with the solutions of sodium dioxide and potassium tetroxide. The apparatus used was essentially that used by Bach: The reaction-flask was kept in a bath of ice-water at 0°. It was fitted with a two-hole rubber stopper, through which passed the burette containing permanganate and a capillary tube connected with a gas-burette. The gas evolved was measured at room temperature and the proper corrections then applied. The permanganate was allowed to drop slowly into the solution, so that there was no rise in temperature.

I. 2 cc. of a solution of commercial hydrogen dioxide were added to 0.6 cc. normal sulphuric acid (calculated amount 0.53 cc., the amount of free acid in the solution having been found to be inconsiderable) and treated with permanganate as just described. At the end of the reaction the flask was shaken until the gas volume became constant.

	cc.
Oxygen evolved (corrected)	9.53
N/10 $KMnO_4$ used	8.8
Oxygen calculated from $KMnO_4$	9.85

II. The previous experiment was repeated except that 3 cc. normal sulphuric acid were used.

	cc.
Oxygen evolved (corrected)	9.54
N/10 $KMnO_4$ used	8.75
Oxygen calculated from $KMnO_4$	9.79

III. 2 cc. pure distilled hydrogen dioxide solution were added to 3.2 cc. of N/5 sulphuric acid (calculated amount 3.02 cc.) and treated as before.

	cc.
Oxygen evolved (corrected)	10.9
N/10 $KMnO_4$ used	10.1
Oxygen calculated from $KMnO_4$	11.3

It will be seen that in all cases the oxygen evolved is from 0.3 to 0.4 cc. lower than the calculated amount. This deficiency is just accounted for by the solubility of oxygen in the solution.

Potassium Tetroxide.

Bach prepared his potassium tetroxide by heating metallic potassium in a silver boat placed in a combustion-tube and heated first in a current of dry air, and finally in oxygen. The product was an orange-yellow, crystalline mass. No further details are given concerning the preparation of the substance, nor was an analysis made. He states that the product was mixed with particles of black silver, which are objectionable on account of their catalytic influence upon the solution.

I attempted to prepare the tetroxide in a flask of hard glass heated in an air-bath at 250°, a current of dry air being passed through the flask. During the oxidation the product spread itself over the entire surface of the flask and consisted of a thin cake, difficult to remove. I have had much better success by using a boat of aluminium, as was done by Erdmann and Köthner[1] in the preparation of the corresponding rubidium compound. During the process of oxidation the aluminium was apparently unaffected and there was no trace of aluminium in the product. The oxidation was carried on in a long glass tube placed in a combustion furnace. The boat containing the potassium was placed quickly in the tube which had been previously swept out with a current of dry air. It was then heated gradually during the passage of the current of dry air. At first the surface of the metal became coated, and this coating did not break until a temperature of 250° was reached. At this point the molten metal spread itself over the bottom of the boat and oxygen was rapidly absorbed. The oxidation was allowed to progress slowly at a temperature of 250° to 300°. The oxidation began in the forward part of the boat, where most of the oxide collected as a crystalline growth about the sides of the boat. After the oxidation had extended the entire length of the boat, the passage of air was continued for an hour or two longer, until the absorption of oxygen had practically ceased (Product A). Another sample of the tetroxide was made in the same way except that it was finally treated with a current of dry oxygen for several hours (Product B). The products were removed by allowing the boat to slide from the combustion tube into a long test-tube which had been swept out with a current of dry air. The tetroxide was easily detached from the sides of the boat by means of a glass rod, and, after removing the boat, was pulverized with the glass rod so as to make it homogeneous. It was then transferred quickly to a smaller tube and preserved in a desiccator.

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[1] *Loc. cit.*

Analysis of Products.—Two methods of analysis were employed:

(1) A weighed amount of the peroxide was introduced into a perfectly dry flask, a pinch of platinum black added, and the flask then connected with a two-hole rubber stopper, through which passed a burette containing dilute sulphuric acid, and a capillary tube leading to a gas-burette. A definite volume of dilute sulphuric acid was then allowed to drop into the flask, sufficient to more than neutralize the solution. The flask was then agitated until there was no further increase in the volume of the gas evolved. In this way all of the oxygen in excess of the monoxide, K_2O, was removed as gas, measured, and the proper corrections applied.

(2) A weighed amount of the peroxide was treated with water, a pinch of platinum black added, and the solution agitated for a few moments while heating on a water-bath. The hydrogen dioxide in the solution was thus removed and the alkali estimated by titrating with N/10 hydrochloric acid. In this way the amount of monoxide, K_2O, was obtained, the difference between this and the weight used being the amount of oxygen disengaged.

Product A.

		Per cent of disengaged oxygen.
0.0700	gram substance gave 0.02135 gram oxygen	30.5
0.0610	" " " 0.01839 " "	30.15
0.0439	" " required 6.5 cc. N/10 HCl	30.19
0.0563	" " " 8.3 " " "	30.49

Product B.

		Per cent of disengaged oxygen.
0.0689	gram substance required 9.85 cc. N/10 HCl	32.60
0.0529	" " " 7.55 " " "	32.71
0.0854	" " gave 0.0282 gram oxygen	33.02

These two methods not only serve as a check upon each other, but their agreement proves that the products consist purely of compounds of potassium and oxygen. The calculated per cent of "per" oxygen or oxygen in excess of the monoxide, K_2O, is:

	Per cent.
For K_2O_4	33.73
" K_2O_3	25.34

The per cent of "per" oxygen in product (B) approaches very closely to the theoretical for the tetroxide, K_2O_4. Both products probably contain a certain amount of the lower oxides.

The assumption has, of course, been made that all oxygen in excess of the monoxide, K_2O, was capable of being disengaged. The agreement of the two methods of analysis shows that this is a fact.

Erdmann and Köthner[1] have expressed doubt whether the ultimate oxidation-product of potassium is represented by the formula K_2O_4, but in view of the analysis of product (B), there can be little doubt on this point. The difficulty in obtaining complete oxidation is probably because small portions of the incompletely oxidized product become covered and protected against further oxidation.

Examination of Solution of Potassium Tetroxide.

I. 0.89 gram of product (A) was dissolved in 13.5 cc. of normal sulphuric acid (calculated amount for neutralization, 13.3 cc.). The substance was added slowly to the cooled solution, the temperature of which was not allowed to rise above 0°.

(*a*) 2 cc. of this solution were added to a large excess of normal sulphuric acid, cooled to 0°, and the solution titrated with N/10 permanganate, the temperature of the solution being kept below 0°. Required, 17.6 cc.

(*b*) 2 cc. were added to an excess of normal sulphuric acid at room temperature and titrated with N/10 permanganate without cooling. Required, 17.6 cc.

(*c*) 2 cc. were added to an excess of normal sulphuric acid containing potassium iodide, the acid solution having been cooled to 0° before the addition. The iodine liberated was estimated by means of N/10 thiosulphate, the temperature of the solution not having been allowed to exceed 0°. Required, 17.7 cc.

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[1] *Loc. cit.*

(*d*) 2 cc. were added to ice-water containing 5.6 cc. N/5 sulphuric acid (calculated amount, 5.3 cc) and titrated with N/10 permanganate as in (*a*). Required 17.7 cc.

(*e*) 1 cc. was added to 2.8 cc. N/5 sulphuric acid (calculated amount, 2.64 cc.) and titrated with permanganate at 0°, in the manner already described under the experiments with pure hydrogen dioxide.

	cc.
Oxygen evolved (corrected)	9.53
N/10 $KMnO_4$ used	8.8
Oxygen calculated from $KMnO_4$	9.85

(*f*) Experiment (*e*) was repeated.

	cc.
Oxygen evolved (corrected)	9.48
N/10 $KMnO_4$ used	8.8
Oxygen calculated from $KMnO_4$	9.85

(*g*) After the tetroxide solution had stood for one hour at 0°, 2 cc. were again titrated with permanganate as in (*b*). Required, 17.8 cc.

During this time there had been no visible evolution of oxygen from the original solution.

(*h*) 2 cc. were added to a like volume of a strong solution of potassium iodide in sulphuric acid. As the liberation of iodine progressed, not a trace of oxygen was evolved from the solution.

II. 1.027 grams of product (B) were dissolved in 15 cc. of normal sulphuric acid (calculated amount, 14.63 cc.) at 0°, as in I., with product (A). With this solution the experiments just described with the solution of product (A) were repeated with the same general results. The results alone are given, as the experiments were carried out in exactly the same way as the corresponding ones given under I.

(*a*) Required 18.7 cc. N/10 $KMnO_4$.
(*b*) " 18.8 " " "
(*c*) " 18.6 " " thiosulphate.
(*d*) " 18.7 " " $KMnO_4$ (11.5 cc. N/10 H_2SO_4 used).

(*e*) 1 cc. of solution added to 2.9 cc. N/5 H_2SO_4 (calculated amount, 2.8 cc.). Required, 9.4 cc. N/10 $KMnO_4$.

	cc.
Oxygen found (corrected)	10.15
Oxygen calculated from $KMnO_4$	10.52

It is evident that the amount of oxygen evolved from this solution by treatment with permanganate bears the same relation to the amount of permanganate used as with the solution of pure hydrogen dioxide. In these experiments the minimum quantity of acid was used, for it has already been shown that with less than the calculated quantity of acid the results are worthless.

Also in stability and in the ratio between its oxidizing value and its reducing value the solution shows exactly the behavior of a solution of hydrogen dioxide. There is, therefore, no reason for assuming the presence of any other substance. We may, therefore, consider the solution of potassium tetroxide to take place in the following way:

$$K_2O_4 + H_2SO_4 = K_2SO_4 + H_2O_2 + O_2.$$

According to this equation only one-third of the "per" oxygen would remain in the solution. The following experiments show this to be approximately true. The results are to be considered as only approximate, because the peroxide (sample B) contained a small amount of lower oxides of unknown nature, and also because the hydrogen dioxide may have been decomposed to a certain extent by local heating.

0.0755 gram was added slowly to an excess of dilute sulphuric acid cooled to 0°. The hydrogen dioxide was estimated with N/10 permanganate, of which 10.45 cc. were required, representing 0.00837 gram active oxygen. One-third of the total amount of "per" oxygen (32.8 per cent) is 0.00825 gram.

0.1390 gram, dissolved as before, required 19.7 cc. N/10 permanganate. The active oxygen, as hydrogen dioxide, is 0.01574 gram. Calculated, 0.01519 gram.

Harcourt[1] has obtained similar numbers by dissolving potassium tetroxide in dilute acid, although the solution was not cooled.

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[1] *Loc. cit.*

Sodium Dioxide.

Bach has also studied a solution of commercial sodium dioxide and obtained results similar to those obtained with the solution of potassium tetroxide. These results I have likewise been unable to verify. A sample of sodium dioxide obtained from Schuchardt, and which had not been previously opened, was used.

Analysis.—0.1243 gram was dissolved in water and the alkali estimated as with potassium tetroxide. 31.2 cc. N/10 HCl were required. Calculated for Na_2O_2, 31.8 cc.

0.1255 gram was dissolved in cold dilute sulphuric acid and the active oxygen estimated by means of potassium iodide and N/10 thiosulphate. Required, 30.3 cc. Calculated for Na_2O_2, 32.1 cc. Bach made no analysis of the sample which he used.

I. 2.5 grams were dissolved in 92 cc. of 1.09 normal sulphuric acid, the temperature being kept at 0° during the solution. (The calculated amount of 1.09 normal acid to dissolve and carry out the reaction with permanganate is 91 cc., based upon the analysis of the product.) Two cc. of this solution were removed and titrated with permanganate at 0°, as previously described.

	cc.
Oxygen evolved (corrected)	13.5
N/10 $KMnO_4$ used	12.4
Oxygen calculated from $KMnO_4$	13.88

II. 2.5 grams were dissolved in 100 cc. of 2.9 normal sulphuric acid which was kept at 0°. Two cc. of this solution gave:

	cc.
Oxygen (corrected)	13.48
N/10 $KMnO_4$ used	12.25
Oxygen calculated from $KMnO_4$	13.88

It is evident that exactly the same amount of oxygen was evolved as from a solution of hydrogen dioxide. From the solution of sodium dioxide Bach obtained an amount of oxygen which was 17 per cent higher than the amount calculated from the permanganate used.

It is possible that Bach's results are to be accounted for by the use of insufficient acid. With potassium tetroxide he used 50 cc. of normal acid to dissolve 3 grams. Whether more acid was added before the treatment with permanganate he does not say, and whether more is necessary cannot be told without knowing the purity of the tetroxide. An analysis of the latter is not given. Three grams of pure potassium tetroxide require 42.1 cc. of normal acid to neutralize the base. 25.3 cc. additional are necessary to carry out the reaction with permanganate, if the substance dissolves according to the equation previously given. This makes a total of 67.4 cc. necessary, while only 50 cc. were used.

With sodium dioxide, 100 cc. normal acid were used to dissolve 5 grams. If the dioxide were pure it would require 128 cc. of the same acid merely to neutralize it, and unless more acid were added before the treatment with permanganate the results would be worthless.

I have previously pointed out, under experiments with pure hydrogen dioxide, the result of the action of permanganate in the presence of insufficient acid. Granting that an insufficient quantity of acid was used, the excess of oxygen obtained by Bach was due to the catalytic action of the precipitated manganese dioxide upon the hydrogen dioxide remaining in the solution.

LABORATORY OF GENERAL CHEMISTRY,
UNIVERSITY OF MICHIGAN,
January 16, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CI.—ON DOUBLE AND TRIPLE THIOCYANATES OF CAESIUM, COBALT, AND SILVER.

BY F. L. SHINN AND H. L. WELLS.

As a continuation of some investigations by one of us and others on complex thiocyanates,[1] we have made a study of the caesium-cobalt, cobalt-silver, and caesium-cobalt-silver salts. The result is that we have found but a single compound in each case, although efforts were made to produce other combinations. The salts to be described are as follows:

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[1] This JOURNAL, 28, 254-284.

$Cs_2Co(SCN)_4.2H_2O$, color blue ;
$CoAg(SCN)_3.2H_2O$, color very dark-blue ;
and $Cs_2CoAg_2(SCN)_6.2H_2O$, color pink.

It is to be noticed that the first of these salts agrees in type with two double salts described in the previous communication from this laboratory, *viz.*,

$Cs_2Mg(SCN)_4.2H_2O$,
and $Cs_2Zn(SCN)_4.2H_2O$.

The cobalt-silver salt, however, does not correspond in type with the following bivalent metal-silver thiocyanates described in the article referred to :

$ZnAg_2(SCN)_4$;
$BaAg_2(SCN)_4.2H_2O$;
$SrAg_2(SCN)_4.2H_2O$;
and $CaAg_2(SCN)_4.2H_2O$.

The triple salt containing cobalt corresponds to the most common type of triple thiocyanates, of which the following were previously described :

$Cs_2CaAg_2(SCN)_6.2H_2O$;
$Cs_2MgAg_2(SCN)_6.2H_2O$;
$Cs_2MnAg_2(SCN)_6.2H_2O$;
$Cs_2NiAg_2(SCN)_6.2H_2O$;
and $Cs_2NiCu_2(SCN)_6.2H_2O$.

The pink color of the new triple salt, as compared with the intense blue colors of the two double salts, which are also hydrous, is worthy of attention, since this color shows that neither of the double salts probably exists as a component part of the triple salt. This argument strengthens the conclusion, reached in the previous article, that the triple salts are not compounds of two double salts.

EXPERIMENTAL PART.

For the work here described a solution of cobalt thiocyanate was prepared by dissolving cobalt carbonate in dilute thiocyanic acid. The latter was obtained by suspending lead thiocyanate (made by precipitation) in water, passing hydrogen sulphide into the liquid, filtering, and removing the excess of hydrogen sulphide by means of a current of air. The methods for preparing caesium thiocyanate have been mentioned in the previous article.

Caesium-Cobalt Thiocyanate, $Cs_2Co(SCN)_4.2H_2O$.—A solution containing about 40 grams of cobalt thiocyanate and gradually increasing quantities of caesium thiocyanate gave no crystals upon concentration, cooling and standing, until about 20 grams of the caesium salt had been added, when large, deep-blue crystals were obtained from a very syrupy solution (Analysis I.). A solution of 50 grams of caesium thiocyanate, to which cobalt thiocyanate was added in small portions, gave crystallizations of a blue salt which had the same appearance as the product mentioned above, but the crops were contaminated with crystals of caesium thiocyanate until about 35 grams of cobalt thiocyanate had been added, when a satisfactory crop was obtained (Analysis II.). Another sample was obtained from a solution containing about equal quantities of cobalt and caesium thiocyanates (Analysis III.). The results of the analyses are as follows:

	Calculated for $Cs_2Co(SCN)_4.2H_2O$.	Found.		
		I.	II.	III.
Cs	44.85	44.35	....	....
Co	9.95	10.00	9.97	10.09
SCN	39.12	39.32	....	....
H_2O	6.07	....	....	....

Cobalt was determined as the metal by electrolysis of the ammoniacal sulphate solution. The caesium in the solution was then determined as sulphate. Sulphocyanogen was determined in a separate portion by the usual volumetric method.

The salt is stable in the air. When they are pulverized, the deep-blue crystals become brighter in color, and the powder loses water somewhat above 100° and becomes green. The anhydrous substance melts at about 170°.

Cobalt-Silver Thiocyanate, $CoAg(SCN)_3.2H_2O$.—This salt was obtained by saturating a hot, very concentrated solution of about 40 grams of cobalt thiocyanate with silver thiocyanate and cooling. Only about 4 grams of the silver salt could be dissolved in this operation, and when smaller quantities of it were dissolved no double salt was obtained. Two separate crops were made and analyzed, with the following results:

	Calculated for $CoAg(SCN)_3.2H_2O$.	Found.	
		I.	II.
Co	15.65	16.30	16.10
AgSCN	44.03	42.90	42.43
Sol. SCN	30.77	30.86	30.81
H_2O	9.55	....	....

For analysis the salt was decomposed by water, the resulting silver thiocyanate was collected and weighed in a Gooch crucible, and the cobalt in the filtrate was determined by the electrolysis of the ammoniacal sulphate solution. Sulphocyanogen was determined volumetrically. The results on cobalt came somewhat high and those on silver low, probably on account of the great excess of cobalt thiocyanate in the liquids from which the products were deposited.

The salt forms small, brilliant crystals which are stable in the air and appear black by reflected light, but show a deep-blue color by transmitted light. The powder has a brilliant blue color. It loses water below 100° and changes its color to dark-green. It may be mentioned here that the simple salt, cobalt thiocyanate, undergoes very striking changes in color when its solution is evaporated to dryness. The dilute solution is pink, the concentrated solution is bright-blue, while the dry salt is yellowish-brown. The last color, which is remarkable for a cobalt salt, is mentioned by Meitzendorff.[1]

Caesium-Cobalt-Silver Thiocyanate, $Cs_2CoAg_2(SCN)_6.2H_2O$. —When a concentrated solution containing about 20 grams of cobalt thiocyanate and 5 grams of the caesium salt was saturated with silver thiocyanate, only 2 or 3 grams of the latter went into solution, and no triple salt was formed upon cooling. However, when the amount of caesium thiocyanate in such a solution was increased to about 10 grams the triple salt was formed, and it continued to be produced, and was evidently more difficultly soluble in the liquid as the caesium salt was gradually increased to 35 grams.

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[1] Pogg. Ann., **56**, 77 (1842).

Three crops, made under different conditions, gave the following results upon analysis :

	Calculated for $Cs_2CoAg_2(SCN)_6.2H_2O$.	Found. I.	II.	III.
Cs	28.75	....	29.12	....
Co	6.38	6.55	....	6.99
AgSCN	35.89	35.22	35.12	35.08
Sol. SCN	25.08	25.20	....	25.16
H_2O	3.90	....	....	....

The salt forms thin, elongated plates of a bright-pink color. The color becomes somewhat violet when the crystals are air-dried, but there is no loss in brilliancy or transparency. The salt readily loses water considerably below 100°, changing its color to a dull dark-green. The anhydrous substance melts in the neighborhood of 180° to a transparent, bright-green liquid, which becomes dull violet upon solidifying and cooling. The salt is only slowly attacked by water, but after a time is completely decomposed by boiling water. It is very difficultly soluble in solutions of caesium and cobalt thiocyanates, and it cannot be recrystallized from water without the presence of an excess of these salts.

NEW HAVEN, CONN., Jan., 1903.

Contributions from the Sheffield Laboratory of Yale University.

CII.—ON SOME CONDENSATION-PRODUCTS OF THE PSEUDOTHIOUREAS : SYNTHESIS OF URACIL, THYMINE, AND SIMILAR COMPOUNDS.

BY HENRY L. WHEELER AND HENRY F. MERRIAM.

Urea and thiourea have been shown to undergo condensation with a variety of substances, but apparently no one has attempted to use the simple pseudothioureas in any synthetic process whatever.[1]

The pseudothioureas in question, $HN=C(SR)—NH_2$, ($R=CH_3—$ or $C_2H_5—$), have not been isolated. Their halogen hydride salts result from the addition of alkyl halides to thiourea. These are described as extremely unstable compounds, and Claus[2] states that when the ethyl bromide addition-product is treated with alkali it decomposes into ethyl rhodanide, ammonia, and hydrogen bromide.

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[1] Rathke has shown that their salts give guanidine when boiled with ammonia. Ber. d. chem. Ges., **17**, 309 (1884).

[2] Ann. Chem. (Liebig), **179**, 146 (1875).

In the case of the methyl iodide addition-product, Bernthsen and Klinger[1] found that, with silver oxide, a solution containing a strong base resulted, which gave a blue color to red litmus. This base was supposed to be a hydroxyl compound, $H_2NCSNH_2.CH_3OH$, which, on evaporating in a desiccator, decomposed. The ethyl iodide addition-product, which Claus describes as an exceptionally unstable compound,[2] under similar treatment with silver oxide gave a strong alkaline solution which, on evaporation, contained cyanamide (dicyandiamide). A similar decomposition was observed when the compounds were treated with mercuric oxide.

We have made no attempts to isolate these free pseudothioureas, but, at first, in order to obtain an idea of their stability, we treated the methyl iodide addition-product in aqueous solution with an excess of alkali and benzoyl chloride, and obtained an excellent yield of the corresponding benzoylpseudothiourea,[3] $C_6H_5CON{=}C(SCH_3){-}NH_2$. The ethyl bromide addition-product, on shaking with alkali and phenyl mustard oil, gave a good yield of the phenylpseudodithiobiuret,

$$C_6H_5NHCSN{=}C(SC_2H_5)NH_2.$$

The free pseudothioureas are, therefore, not so unstable as one might be led to believe from previous work, and, owing to their strong basic nature, it seemed probable that they would undergo condensation with aldehyde and ketone esters more readily, and prove more reactive in general, than the normal ureas. This we have found to be the case.

Ernert[4] states that urea does not condense with the substituted acetoacetic esters or with benzoylacetic ester. Warmington,[5] also, was unable to obtain a condensation of urea and the latter ester, in aqueous solution, but found that they could be condensed in the dry state at a high temperature.

We have readily obtained such condensations with the pseudothioureas at ordinary temperatures. These pyrimidine condensations, which are analogous to Pinner's,[1] take place in alkaline solution in a similar manner to that observed by Michael in the case of urea with acetoacetic and malonic esters.[2] They are also similar to Traube's synthesis of pyrimidine derivatives in which guanidine and ethyl cyanacetate are employed.[3]

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[1] Ber. d. chem. Ges., **11**, 493 (1878).

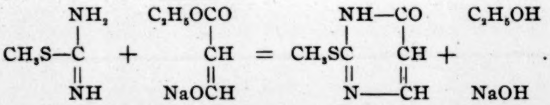
[2] *Ibid.*, **8**, 41 (1875).

[3] J. Am. Chem. Soc., **23**, 293 (1901).

[4] Ann. Chem. (Liebig), **258**, 362 (1890).

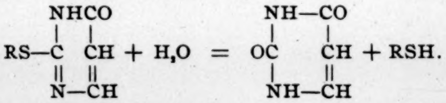
[5] J. prakt. Chem., [2], **47**, 202 (1893).

A method similar to that of preparing methyluracil by condensing urea with acetoacetic ester, by means of hydrochloric acid,[4] has not been applied to the preparation of uracil, probably on account of the ease with which free formylacetic ester passes into trimesic ester. On the other hand, the sodium salt of formylacetic ester is not only easily prepared,[5] but is also quite stable, and we have found that it readily condenses, in aqueous solution, with both methyl- and ethylpseudothioureas, giving a good yield of the corresponding methyl- and ethyl-mercaptouracils. For example, with methylpseudothiourea, as follows :[6]



$$\begin{array}{cccccccc} & NH_2 & & C_2H_5OCO & & NH\text{—}CO & & C_2H_5OH \\ & | & & | & & |\quad\;\; | & & \\ CH_3S\text{—} & C & + & CH & = CH_3SC & \;\; CH & + & \\ & \| & & \| & & \|\quad\;\; \| & & \\ & NH & & NaOCH & & N\text{——}CH & & NaOH \end{array}$$

In order to obtain a practically quantitative yield of uracil from these compounds, heating with acids in a sealed tube is not necessary.[7] When they are boiled with concentrated hydrochloric acid, or better with hydrobromic acid, they evolve mercaptan and yield uracil as follows :



$$\begin{array}{ccccccc} & NHCO & & & & NH\text{—}CO & \\ & |\quad | & & & & |\quad\;\; | & \\ RS\text{—}C & \;\; CH & + H_2O & = & OC & \;\; CH & + RSH. \\ & \|\quad \| & & & & |\quad\;\; \| & \\ & N\text{—}CH & & & & NH\text{—}CH & \end{array}$$

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[1] "Die Imidoäther u. ihre Derivate," p. 209.

[2] J. prakt. Chem., **35**, 456 (1887).

[3] Ber. d. chem. Ges., **33**, 1371 (1900).

[4] Behrend : Ann. Chem. (Liebig), **229**, 9 ; **251**, 238.

[5] Wislicenus : Ber. d. chem. Ges., **20**, 2933 (1887).

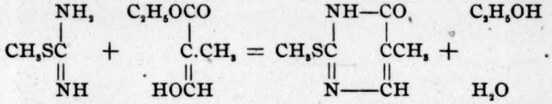
[6] An attempt to condense urea with this salt gave a negative result.

[7] List has shown that 2-methylmercapto-4-methyluracil gives 4-methyluracil when heated with concentrated hydrochloric acid at 180°. Ann. Chem. (Liebig), **236**, 12 (1886).

Emil Fischer and Georg Roeder[1] have recently prepared uracil, thymine, and other pyrimidine derivatives by means of an interesting synthesis. Their method consists in heating urea with unsaturated acids and brominating the hydrouracils thus formed. The bromine derivatives are then converted into uracils by treatment with alkali or pyridine. This synthesis has the disadvantage that the unsaturated acids are not in all cases easily accessible compounds, and the yields, especially in the case of uracil, are below those obtained by our method.

Uracil prepared by our method agreed in all respects with the description given by Fischer and Roeder. We have found that sodium acetoacetic ester and pseudomethylthiourea give 2-methylmercapto-4-methyluracil, which List[2] has prepared by a different method. This, on boiling with hydrobromic acid, gave Behrend's[3] 4-methyluracil.

The isomeric 2-methylmercapto-5-methyluracil and 5-methyluracil, or thymine, were obtained in a similar manner. Free ethyl formylpropionate directly condensed with pseudomethylthiourea, and the sodium salt was also caused to react with the pseudothiourea:



$$\begin{array}{ccccccc} NH_2 & & C_2H_5OCO & & NH-CO & & C_2H_5OH \\ | & & | & & |\quad\;\; | & & \\ CH_3SC & + & C.CH_3 & = & CH_3SC\quad CCH_3 & + & \\ \| & & \| & & \|\quad\;\; \| & & \\ NH & & HOCH & & N-\!\!-CH & & H_2O \end{array}$$

On boiling this mercapto derivative with hydrochloric acid we obtained thymine, which was identical in all respects with the natural product obtained from the nucleic acid of the spleen, a sample of which, through the kindness of Dr. P. A. Levene, was sent to us for comparison. When the samples were mixed the melting-point was not altered.

With the sodium salt of ethyl benzoylacetate and pseudomethylthiourea we obtained 2-methylmercapto-4-phenyluracil, which was converted by acids into 4-phenyluracil, identical with the phenyluracil described by Fischer and Roeder.

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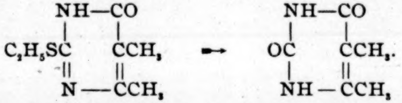
[1] Ber. d. chem. Ges., **34**, 3751 (1901).

[2] Ann. Chem. (Liebig), **236**, 12 (1886).

[3] *Ibid.*, **229**, 8.

With ethyl methylacetoacetate and pseudoethylthiourea we prepared 2-ethylmercapto-4,5-dimethyl-6-oxypyrimidine, which gave a new dimethyluracil (4,5-dimethyluracil):



With ethyl ethyl-acetoacetate we prepared 2-methylmercapto-4-methyl-5-ethyl-6-oxypyrimidine and 4-methyl-5-ethyluracil. Like urea,[1] pseudomethylthiourea readily condenses with acetylacetone and two products are formed. It condenses also with ethyl cyanacetate.

Beside the above condensations, which involve an attachment to the two nitrogen atoms of the pseudothiourea, another type occurs in which only one nitrogen and the mercapto group take part. For example, amino acids react with the pseudothioureas in aqueous solution to form guanidine acids:

$$HN{=}C{-}(NH_2){-}SR + H_2NCH_2COOH = HN{=}C{-}(NH_2){-}NHCH_2COOH + RSH.$$

Since by appropriate treatment these compounds can be converted by loss of water into the corresponding rings, it seems probable that the isocreatinine obtained by Thesen[2] from fish flesh (haddock) may be prepared by this method, using N-methylpseudomethylthiourea and aminoacetic acid.

We wish to reserve the study of the condensation-products of the pseudothioureas for this laboratory.

EXPERIMENTAL PART.

Our experiments with the pseudothioureas have been confined to pseudomethyl- and pseudoethylthiourea.

Pseudomethylthiourea hydriodide was prepared by moistening finely powdered thiourea with alcohol and then adding an excess of methyl iodide. Heat was evolved so that a condenser was necessary. After standing twelve hours, ether was added and the residue filtered, washed with ether, and dried. The crude addition-product thus prepared was used in the following experiments.

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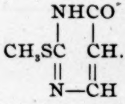
[1] Evans: J. prakt. Chem., 48, 489 (1893).

[2] Hoppe-Seyler: Ztschr. physiol. Chem., 24, 4 (1898).

Pseudoethylthiourea hydrobromide, for use in these condensations, can be conveniently prepared from thiourea containing considerable ammonium thiocyanate; that is to say, from the product obtained by heating ammonium thiocyanate at 170° for forty-five minutes[1] and then crystallizing once or twice from water. The thiourea is powdered, moistened with alcohol, and an excess of ethyl bromide added. On boiling this mixture for four or five hours the greater part of the mass dissolves, leaving ammonium bromide as an insoluble residue. The solution is then filtered and most of the alcohol evaporated. The oil thus obtained is transferred to a distilling-bulb and the ethyl rhodanide distilled off under diminished pressure on the water-bath. The residue, on cooling, solidifies to a crystalline mass, which, after drying on paper in the air, melts at about 88° and is pure enough for use in the following experiments:

2-Methylmercapto-6-oxypyrimidine,



$$\begin{array}{ccc} & \text{NH} & \text{CO} \\ & | & | \\ \text{CH}_3\text{S} & \text{C} & \text{CH}. \\ & \| & \| \\ & \text{N} & \text{—CH} \end{array}$$

— In this preparation the crude sodium salt of formylacetic ester[2] was considered as 70 per cent pure.[3]

Seven grams of sodium hydrate were dissolved in 70 cc. of water and 38 grams of the methyl iodide addition-product of thiourea were added, and then 29 grams of sodium formylacetic ester. The mixture was allowed to stand for twelve hours at ordinary temperature, then warmed on the water-bath for a few minutes, cooled, and acidified with acetic acid. The crystalline precipitate thus produced was filtered, washed, and dried. It weighed 11.3 grams, a yield of 46 per cent, calculating from the methyl iodide addition-product. It crystallized from water in long prisms, or short, lozenge-shaped tablets, and the surfaces of the crystals were generally etched. It is quite soluble in alcohol and acetone, and it melts at 198° to 199°. A nitrogen determination gave :

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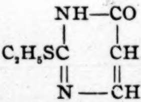
[1] Reynolds and Werner: J. Chem. Soc. (London), 83, 1 (1903).

[2] Wislicenus: Ber. d. chem. Ges., 20, 2933.

[3] Von Pechmann: *Ibid.*, 25, 1047.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.72	19.86

2-Ethylmercapto-6-oxypyrimidine,



$$\begin{array}{rcl} \mathrm{NH} & — & \mathrm{CO} \\ | & & | \\ \mathrm{C_2H_5SC} & & \mathrm{CH.} \\ \| & & \| \\ \mathrm{N} & — & \mathrm{CH} \end{array}$$

— Fifty-nine grams of the ethyl bromide addition-product of thiourea were treated with one molecular proportion of sodium hydrate in 10 per cent aqueous solution, and then 40 grams of formylacetic ester were added. After standing for twenty-four hours the solution was divided into two equal portions. One, after warming on the water-bath until effervescence stopped, was cooled and immediately acidified with acetic acid. This gave 6.3 grams of the mercapto derivative. The other portion was allowed to stand for a week. On acidifying then, 6.1 grams of the mercapto compound were obtained, a yield of 32 per cent of the calculated. In another experiment 25 grams of the ethyl bromide addition-product were dissolved in more dilute alkali, namely, 5.5 grams of sodium hydrate in 95 cc. of water, and 27 grams of sodium formylacetic ester were added. After two hours' standing, one-half of the solution was warmed, cooled, and acidified with acetic acid, whereupon 5 grams of the mercapto compound separated. After standing two days the remaining portion gave 4.9 grams of the condensation-product, a yield of 47 per cent of the calculated.

It is evident from this that the materials react in a short time, and that long standing does not influence the yield. The reaction possibly involves an addition similar to that in the case of acetoacetic ester and urea[1], since it frequently happens that these mixtures can stand for several days, and then, if the solution is not warmed before acidifying, no precipitation whatever occurs. Moreover, the fact that usually a yield approximating only one-half the calculated is obtained may also possibly be accounted for by the assumption that, like urea and acetoacetic ester in alkaline solution, 2 molecules of the ester react with only one of the pseudothiourea.

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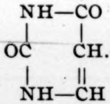
[1] Behrend and Ernert: Ann. Chem. (Liebig), **258**, 360 (1890).

In one experiment, however, 5 grams of the ethyl bromide addition-product, 1.1 grams of sodium hydrate, and 6 grams of the sodium salt in 10 cc. of water, on standing over night, gave 2.9 grams of the condensation-product, a yield of 68.8 per cent of the calculated. On crystallizing from 10 cc. of alcohol, 1.75 grams of pure ethylmercaptooxypyrimidine separated at once. This substance is easily soluble in warm alcohol and hot water, difficultly soluble in cold, and forms beautiful, colorless, small, stout prisms and pyramids melting at 152°. A nitrogen determination gave:

	Calculated for $C_6H_8ON_2S$.	Found.
N	17.94	17.93

Uracil, .—Fifteen grams of the above methylmercaptouracil and 150 cc. of concentrated hydrochloric acid were boiled for four hours, when mercaptan had ceased being evolved. The solution was evaporated to dryness and the residue, after drying, weighed 11.9 grams (94.4 per cent yield). It melted with effervescence at 335° (on an Anschütz thermometer in a paraffin-bath), and, on crystallizing from water, it formed balls of minute, pure-white needles, which, on rapidly heating, melted at 338°. By holding the temperature a few degrees below this the material could be made to melt. It agreed in properties with Fischer and Roeder's[1] preparation. When the ethylmercapto derivative (1.5 grams) was heated in a closed tube with concentrated hydrochloric acid (5 cc.) for four and one-half hours, about 0.05 gram of an insoluble by-product was formed, and 0.9 gram of pure uracil was obtained. A nitrogen determination gave:

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[1] *Loc. cit.*

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	25.24

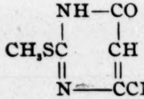
One hundred parts of water at 25° dissolve 0.358 part of uracil.

Uracil may be boiled with alkali and recovered unaltered by acidifying the solution. The alkaline solution probably contains the substance as a salt of β-uramidoacrylic acid, just as Behrend's methyluracil gives β-uramidocrotonic acid. When uracil is dissolved in ammonia and most of this removed by boiling, then silver nitrate is added and the solution is boiled, an amorphous silver salt is precipitated, which is soluble in an excess of ammonia and nitric acid. The composition of the salt prepared in this manner varied. One preparation gave 63.8 and 64 per cent silver, another 59.9 and 60.1 per cent silver, while the calculated for silver β-uramidoacrylate is 62.79 per cent. Uracil does not form a picrate.

5-Bromuracil.—Two and one-half grams of uracil were suspended in carbon disulphide and 3.8 grams of bromine were added. Hydrogen bromide was slowly evolved, and after two days, on evaporating to dryness, a red residue was obtained which, on warming on the water-bath, became colorless. When crystallized from water it formed small, stout, colorless prisms, and when heated turned dark above 200°, and melted with some effervescence at about 293°. A nitrogen determination gave:

	Calculated for $C_4H_3O_2N_2Br$.	Found.
N	14.66	14.60

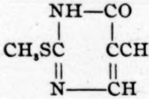
2-Methylmercapto-4-methyl-6-oxypyrimidine,



$$\begin{array}{lll} & NH-CO & \\ & | \quad\quad | & \\ CH_3SC & & CH \\ & \| \quad\quad \| & \\ & N=CCH_3 & \end{array}$$

.—Sixteen grams of the methyl iodide addition-product of thiourea were dissolved in 20 cc. of water and added to a cold 30 per cent solution of 4.5 grams of potassium hydrate. Nine and six-tenths grams of acetoacetic ester were then added and the mixture allowed to stand. The next day long prisms had formed. After two days these were filtered and found to weigh 5 grams. This material was soluble in acids and alkali, and it melted at 219°, the melting-point assigned to this compound by List. When 2 grams of this were boiled with 10 cc. of hydrobromic acid for one hour mercaptan was given off and 1.2 grams of Behrend's 4-methyluracil were obtained.

2-Methylmercapto-5-methyl-6-oxypyrimidine,

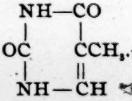


$$\begin{array}{lcl} \mathrm{NH} & - & \mathrm{CO} \\ | & & | \\ \mathrm{CH_3SC} & & \mathrm{CCH_3} \\ \| & & \| \\ \mathrm{N} & - & \mathrm{CH} \end{array}$$

—Sixty-five grams of the methyl iodide addition-product of thiourea were treated with 17 grams of potassium hydrate in 150 cc. of water, and 45 grams of sodium formylpropionic ester were then added. The mixture, on standing two and a half days, was filtered from some sediment and neutralized with acetic acid. A fine crystalline precipitate of methylmercaptothymine came down, which weighed 9.2 grams, or 20 per cent of the calculated. It crystallized in strings of small plates from water, in which it is difficultly soluble when hot and nearly insoluble when cold. On heating, it sintered at about 225° and melted at 233°. A nitrogen determination gave:

	Calculated for $C_6H_8ON_2S$.	Found.
N	17.94	17.95

5-Methyluracil (*Thymine*),



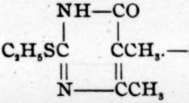
$$\begin{array}{lcl} \mathrm{NH} & - & \mathrm{CO} \\ | & & | \\ \mathrm{OC} & & \mathrm{CCH_3} \\ | & & \| \\ \mathrm{NH} & - & \mathrm{CH} \end{array}$$

—The above mercaptothymine reacted less readily with hydrochloric acid than in the other cases. Nine and two-tenths grams were boiled with 100 cc. of concentrated hydrochloric acid for ten hours, whereupon no more mercaptan was given off. The solution, on evaporating, then gave 7.3 grams of crude thymine (melting at 319°), which is 99 per cent of the calculated. This crystallized from water in small, apparently rectangular, colorless plates, and on rapidly heating melted at 326° (on an Anschütz thermometer). Fischer and Roeder state that their preparation sintered at 318° and melted at 321°. A sample of thymine which Dr. P. A. Levene, of the Pathological Institute at Ward's Island, N. Y., kindly gave us, proved to be identical with our compound. This sample was obtained from the nucleic acid of the spleen, and on mixing it with some of our substance the melting-point was unchanged. A nitrogen determination in the case of the synthetic product gave:

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.36

One hundred parts of water at 25° dissolve 0.404 part of thymine.

2-Ethylmercapto-4,5-dimethyl-6-oxypyrimidine,



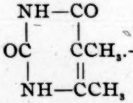
—Six grams of potassium hydrate were dissolved in 50 cc. of water and cooled. To this was added 13 grams of the ethyl bromide addition-product of thiourea and then 10 grams of methyl acetoacetic ester. The oil gradually disappeared and a white solid was formed. After standing for two days the solution was made slightly acid with hydrochloric acid and filtered. The precipitate in this case proved to be a mixture. On boiling with about 30 cc. of alcohol and filtering while hot, a separation was effected. The soluble portion was crystallized from a mixture of alcohol and ether. It formed stout prisms melting at about 156°, sintering at about 151,° and a nitrogen determination gave:

	Calculated for $C_8H_{12}ON_2S$.	Found.
N	15.2	15.6

The compound that was not readily dissolved by boiling alcohol was purified by crystallizing it from a large amount of alcohol. It was found to be free from sulphur, and on heating it began to decompose at about 260°, and effervesced at 269° to 270°, turning reddish-brown. It consisted of minute, microscopic crystals that formed twins having the form of a cross. We did not stop to determine the structure of this compound, but we believe that possibly it is acetomethylacetylcyanamide, $CH_3CO(CH_3)CHCONHCN$. A nitrogen determination agreed with the calculated for this formula.

	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.03

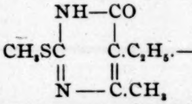
4.5-Dimethyluracil,



—About 1 gram of the above ethylmercaptodimethyluracil was boiled for four hours with 10 cc. of concentrated hydrochloric acid. Mercaptan was given off and there was a smooth decomposition into the oxygen derivative. The solution was evaporated to dryness and the residue was crystallized twice from alcohol. It crystallized in microscopic needles which melted to a clear liquid, with partial decomposition, at 292°. A nitrogen determination gave:

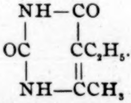
	Calculated for $C_6H_8O_2N_2$.	Found.
N	20.00	20.34

2-Methylmercapto-4-methyl-5-ethyl-6-oxypyrimidine,



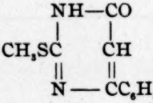
—Ten grams of the methyl iodide addition-product of thiourea were dissolved in a solution of 2.6 grams of potassium hydrate (1 molecule) in 20 cc. of water, and to this 7 grams of ethyl ethylacetoacetate were added. A little alcohol was also added, and finally some more alkali, and the mixture was allowed to stand for a week. Solid material gradually separated, which was filtered after neutralizing the solution. The yield of crude material was 3.2 grams. It was crystallized from alcohol, from which it separated in long, flat, colorless prisms with branching, brush-like ends. It sintered at 201° to 202° and melted at about 203° with slight effervescence. It was fairly soluble in hot alcohol and very difficultly soluble in water. A nitrogen determination gave:

	Calculated for $C_8H_{12}ON_2S$.	Found.
N	15.22	15.26

4-Methyl-5-ethyluracil,  .—When the above was boiled for three hours with hydrobromic acid and evaporated a syrup was obtained, which solidified on treating with alcohol. After six crystallizations from alcohol it melted constantly at 237°, sintering at about 230°. It formed irregular, colorless leaflets. A nitrogen determination gave:

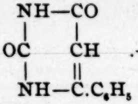
	Calculated for $C_7H_{10}O_2N_2$.	Found.
N	18.18	17.86

2-Methylmercapto-4-phenyl-6-oxypyrimidine,



.—Fifteen grams of the methyl iodide addition-product of thiourea were dissolved in a solution of 8 grams of potassium hydrate in 40 cc. of water, and 12 grams of benzoylacetic ester were then added. After the mixture was allowed to stand for two days it was acidified and the precipitate crystallized from alcohol, whereupon 3.5 grams of material crystallizing in long, slender needles, melting at 240°, were obtained. A nitrogen determination gave:

	Calculated for $C_{11}H_{10}ON_2S$.	Found.
N	12.89	12.74

4-Phenyluracil,  .—A small amount of the above methylmercaptophenyloxypyrimidine was heated with concentrated hydrochloric acid for two hours. It gradually went into solution and then separated in crystalline form. The solution was evaporated to dryness and the residue was crystallized from alcohol. The crystals were in the form of microscopic prisms and melted at 269° to 270°. Fischer and Roeder state that their phenyluracil formed microscopic needles melting at 267° (corr.).

Guanidineacetic acid[1] (*Glycocyamine*) was formed when 12.2 grams of the methyl iodide addition-product of thiourea were dissolved in 15 cc. of water containing 3.2 grams of potassium hydrate, and then a concentrated solution of 5 grams of amidoacetic acid were added. Mercaptan began to come off immediately, the mixture evolved heat, and crystals separated. These were fairly soluble in water, and formed rectangular plates which decomposed between 250° to 260° without melting. A nitrogen determination gave:

	Calculated for $C_3H_7O_2N_3$.	Found.
N	35.89	36.07

The *picrate* separated from an aqueous solution in long, bright-yellow needles, melting with decomposition at about 202°. It was very soluble in hot water and sparingly in cold. A nitrogen determination gave:

	Calculated for $C_9H_{10}O_9N_6$.	Found.
N	24.27	24.00

Orthoguanidinebenzoic acid was obtained when 8 grams of the methyl iodide addition-product of thiourea were added to an aqueous solution of 5 grams of anthranilic acid and 2 grams of potassium hydrate. The material was practically insoluble in water, alcohol, and benzene, and did not melt at 260°. A nitrogen determination gave:

	Calculated for $C_8H_9O_2N_3$.	Found.
N	23.46	23.70

When this substance was dissolved in aqueous sodium hydrate, and precipitated with carbon dioxide, it gave *o*-benzglycocyamidine.[1]

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[1] Strecker: Jsb., 1861, 530; Nencki and Sieber: J. prakt. Chem., [2], 17, 477.

Pseudomethylthiourea Chloracetate, $H_2N—C(SCH_3)=NH.ClCH_2COOH$.—Thirty-three grams of the methyl iodide addition-product of thiourea were dissolved in a small quantity of cool alcohol, and a concentrated alcoholic solution of 8.5 grams of potassium hydrate was added. The solution was filtered from potassium iodide and then 14.5 grams of chloracetic acid were slowly added. Crystalline material soon separated which, on drying, weighed 17 grams. When crystallized from alcohol it formed transparent, rectangular plates, melting at 162°. It was very soluble in water. A nitrogen determination gave:

	Calculated for $C_4H_9O_2N_2SCl$.	Found.
N	15.17	15.26

New Haven, Conn., Feb. 26, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CIII.—SYNTHESES OF AMINOOXYPYRIMIDINES HAVING THE COMPOSITION OF CYTOSINE: 2-AMINO-6-OXYPYRIMIDINE AND 2-OXY-6-AMINOPYRIMIDINE.

By Henry L. Wheeler and Treat B. Johnson.

The interest which in recent years has been attached to the study of pyrimidine derivatives has been increased by a new discovery of Kossel and Steudel. Working with a large quantity of sturgeons' testicles they obtained, in the histidine fraction, a basic substance agreeing in composition with the formula $C_4H_5ON_3$. Kossel and Steudel state their belief that this compound is an aminooxypyrimidine,[2] since hitherto all of the nitrogen compounds obtained from nucleic acid have been found to contain the pyrimidine ring. This new substance was found to closely resemble cytosine, which Kossel and Neumann[3] obtained in the year 1894 as a cleavage-product of thymus nucleic acid. Kossel and Steudel have recently undertaken the reinvestigation of thymus cytosine and they now[1] conclude that the product is identical with sturgeon cytosine. They state that it can also be prepared from herrings' testicles and call attention to the fact of its wide occurrence in animal organs.

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[1] Griess: Ber. d. chem. Ges., **13**, 977.

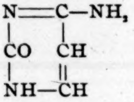
[2] Ztschr. physiol. Chem., **37**, 179 (1902).

[3] Ber. d. chem. Ges., **27**, 2215 (1894).

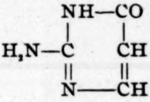
Dr. P. A. Levene has kindly sent us the proof of his article on "Darstellung und Analyse einiger Nucleinsäuren," in which he describes the preparation of this base from the nucleic acid of the spleen and pancreas.[2]

Kossel and Steudel[3] conclude that material yielding uracil is widely disseminated in animal organs, and it seemed probable that perhaps uracil results from the cleavage of cytosine by treatment with sulphuric acid at high temperatures. Moreover, they state in their last paper[4] that cytosine, by the action of nitrous acid, gives a substance having the properties of uracil.

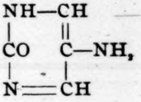
From this it appears that of the seven theoretically possible[5] aminooxypyrimidines, the first to be considered are those that would be expected to yield uracil by the above treatment. An examination of the following formulas will show that formulas I. and II. are the only ones that agree with this behavior :



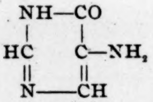
I.



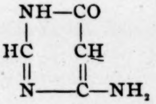
II.



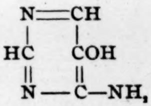
III.



IV.



V.



VI.

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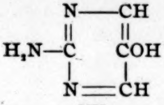
[1] Ztschr. physiol. Chem., **37**, 379 (1903).

[2] To appear in Ztschr. physiol. chem., **38**, (1903). See also Am. J. Physiol., **8**, XII (1903); J. Am. Chem. Soc., **25**, R. 188 (1903).

[3] *Ibid.*, **37**, 247 (1903).

[4] *Ibid.*, **37**, 380 (1903).

[5] Tautomeric forms are not considered.



VII.

We have now prepared the two aminooxypyrimidines represented by formulas I. and II. and we find that both products agree closely in properties with the descriptions of cytosine. Of the two compounds, 2-oxy-6-amino-pyrimidine, formula I., agrees better than the isomer, 2-amino-6-oxypyrimidine. Formula II., in fact, seems to be excluded as representing cytosine chiefly because this compound crystallizes from water in anhydrous crystals. Its picrate melts a little higher than the melting-point given for cytosine picrate, but in other respects the salts are closely similar.

On the other hand, 2-oxy-6-aminopyrimidine crystallizes with 1 molecule of water of crystallization, like cytosine, and its properties agree in practically every respect, as far as can be judged, with the descriptions of the natural substance. The picrate, when prepared from the pure base, has a higher decomposing-point than that given for the picrate from natural cytosine. However, we are inclined to believe that our base and cytosine are identical and, therefore, the structure of cytosine is to be represented by formula I.[1] It will be necessary to compare our material with the natural before this can be definitely settled, and we hope soon to obtain a sample of the natural substance.

When 2-oxy-6-aminopyrimidine was heated with 20 per cent sulphuric acid for 3 hours at 150°-170° it was found that 15 per cent of the material was converted into uracil. Dr. Osborne informs us that to obtain uracil it was necessary to heat triticonucleic acid with acids for a considerable time.[2]

Since uracil results from the cleavage-cytosine, the natural assumption is that the analogous thymine, which until recently has been more widely obtained as a cleavage-product, results from the decomposition of a corresponding base, the as yet undiscovered 5-methylcytosine, this base undergoing cleavage more readily than cytosine. We intend to give an account of this new base later, the preparation of these bases being one of the first steps toward the synthesis of the nucleic acids.

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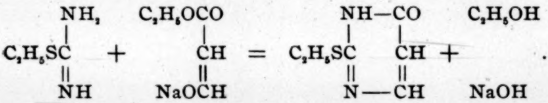
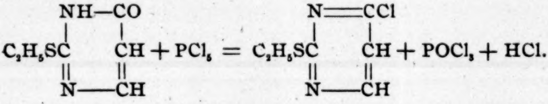
[1] The substance can naturally be viewed as 2-oxy-4-aminopyrimidine, and, on account of the usual nomenclature, this aspect better illustrates its character as a sort of hydrated fragment of uric acid. Its relation to uracil, however, is better shown by representing the substance as a 6-amino derivative or the tautomeric 6-imino form.

[2] See Report Conn. Agr. Expt. Sta. for 1901 p. 409.

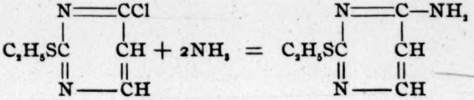
We prepared the synthetic cytosine as follows: The ethyl bromide addition-product of thiourea was treated with 1 molecule of alkali in aqueous solution and the sodium salt of ethyl formylacetate added. On standing a number of hours, then warming for a few minutes, cooling, and acidifying with acetic acid, 2-ethylmercapto-6-oxypyrimidine was obtained:



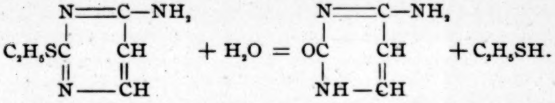
The 2-ethylmercapto-6-oxypyrimidine was converted into 2-ethylmercapto-6-chlorpyrimidine by means of phosphorus pentachloride and the phosphorus oxychloride was removed by evaporation in a vacuum.



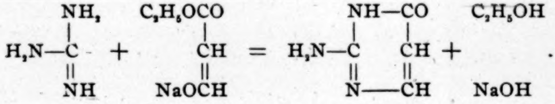
When 2-ethylmercapto-6-chlorpyrimidine was heated with alcoholic ammonia it gave 2-ethylmercapto-6-aminopyrimidine.



Finally the 2-ethylmercapto-6-aminopyrimidine was converted into the 2-oxy-6-aminopyrimidine by boiling with hydrobromic acid:



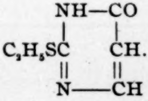
The synthesis of 2-amino-6-oxypyrimidine was effected by treating sodium formylacetic ester with free guanidine in aqueous solution, whereupon the following condensation took place:



Sodium formylacetic ester is easily prepared by treating equal weights of ethyl formate and ethyl acetate, in two volumes of ether, with metallic sodium, according to the directions of Wislicenus.[1]

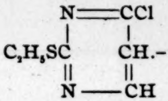
EXPERIMENTAL PART.

2-Ethylmercapto-6-oxypyrimidine,



—This compound has been described in the preceding article by Wheeler and Merriam. We have usually taken 50 grams of the ethyl bromide addition-product of thiourea,[2] dissolved in 10 per cent sodium hydrate, and have then added somewhat over the calculated quantity of dry sodium ethyl formylacetate. After standing for two or three hours the solution, heated to boiling and then cooled, was acidified with acetic acid. A yield of about 48 per cent of the calculated of crude mercaptooxypyrimidine was usually obtained.

2-Ethylmercapto-6-chlorpyrimidine,



—When

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[1] Ber. d. chem. Ges., **20**, 2933 (1887).

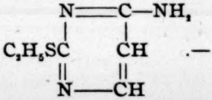
[2] Claus: Ann. Chem. (Liebig), **179**, 145.

2-ethylmercapto-6-oxypyrimidine (5.3 grams) and phosphorus pentachloride (7.5 grams) were warmed on the steam-bath they reacted smoothly and hydrogen chloride was given off. The product was an oil. An attempt to purify it by distilling off the phosphorus oxychloride at ordinary pressure in an oil-bath, at 150°, caused decomposition. It was found that the oil could be distilled in steam, but the greater part was converted into uracil by this treatment. The portion purified in this manner (2 grams) was analyzed with the following result:

	Calculated for $C_6H_7N_2SCl$.	Found.
N	16.04	16.8

The oil, when dry, is stable at 150°. When boiled with hydrochloric acid it gives uracil. The chlorpyrimidine, for conversion into the amino derivative, was prepared as follows: 6.3 grams of 2-ethylmercapto-6-oxypyrimidine and 8.5 grams of phosphorus pentachloride were heated on the steam-bath until the action was complete. The phosphorus oxychloride was removed by heating in an oil-bath at 140°, under a pressure of 12 mm., for about fifteen minutes. The crude oil thus obtained weighed 6.5 grams, a yield of 92 per cent of the calculated. In another preparation 15.5 grams of the 2-ethylmercapto-6-oxypyrimidine gave 15.5 grams of chlorine compound, or 90 per cent of the calculated.

2-Ethylmercapto-6-aminopyrimidine,

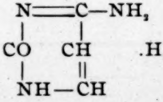


.—When 2-ethylmercapto-6-chlorpyrimidine (6.5 grams) was heated in a closed tube with alcoholic ammonia at 140° to 150°, for six hours, the action was complete. An odor of mercaptan was apparent on opening the tube, showing too energetic treatment, and ammonium chloride had separated. The alcohol was removed by evaporation, after filtering from ammonium chloride, and the dark varnish which was obtained was washed with a few cubic centimeters of cold water. By this treatment the material completely solidified to a hard cake. It was very soluble in alcohol and in benzene, and fairly soluble in hot water. The weight of the crude product was 4.7 grams, a yield of 82 per cent of the calculated. The base dissolved immediately in dilute hydrochloric acid and was precipitated by ammonia in stout tables. It was purified by boiling in alcohol with animal charcoal and then crystallizing from 50 per cent alcohol. It separated in the form of colorless plates and melted at 85° to 86°. A nitrogen determination gave :

	Calculated for $C_6H_9N_3S$.	Found.
N	27.1	27.6

In another preparation the chlorpyrimidine was heated with alcoholic ammonia at 115° to 120° for five and a half hours. From 15.5 grams of the chlorine compound 11.6 grams of the base were obtained, which is a yield of 84 per cent of the calculated.

Cytosine or 2-Oxy-6-aminopyrimidine,



$.H_2O$.—

The above 2-ethylmercapto-6-aminopyrimidine (3 grams) was boiled with hydrobromic acid of boiling-point 125° (15 cc.) for two hours, when mercaptan had ceased being evolved. On evaporating the free hydrobromic acid on the steam-bath a beautiful crystalline mass of the hydrobromide was obtained. It crystallizes in the form of glistening prisms from a little water. The free base was obtained by dissolving the hydrobromide in water and precipitating with ammonia. The weight of the crude base was 1.9 grams, which is a yield of 79 per cent of the calculated. In another experiment 7.5 grams of 2-ethylmercapto-6-aminopyrimidine gave 5.6 grams of 2-oxy-6-aminopyrimidine, or 90 per cent of the calculated. The base for analysis was boiled with animal charcoal and crystallized from water. It was dried in the air and the water of crystallization determined by heating in an oven at 100° to 110°.

0.5166 gram substance lost 0.0727 gram on heating.

	Calculated for $C_4H_5ON_3.H_2O$.	Found.
H_2O	13.95	14.07

The analysis of the dried material gave the following results:

0.2188 gram substance gave 0.3498 gram CO_2 and 0.0835 gram H_2O.

0.0939 gram substance gave 31 cc. moist N at 25° and 773 mm. pressure.

	Calculated for $C_4H_5ON_3$.	Found.
C	43.25	43.60
H	4.50	4.25
N	37.84	37.72

Properties of 2-Oxy-6-aminopyrimidine.—The free base, when first obtained, crystallized from hot water in the form of needle-like prisms. It was then somewhat colored (pale brownish), and melted, or rather decomposed, at 320° to 325° with violent effervescence, first becoming dark-colored a little below 300°. After boiling in aqueous solution with animal charcoal it crystallized in the form of beautiful, colorless, transparent plates. The edge of one of these crystals, which perhaps was made up of a number of plates, measured three-quarters of an inch in length. The faces were so badly etched, or striated, or covered with vicinal growths, that crystallographic measurements were impossible. They probably belong to the mono- or triclinic system. The plates had the same effervescing-point on heating as the needle-like prisms. These decomposing-points were taken in capillary tubes, in a paraffin-bath, on an Anschütz thermometer 13.5 centimeters in length, and are uncorrected. The plates dissolve in about 129 parts of water at 25°. The base is precipitated by phosphotungstic acid. It would, therefore, be found in the histidine fraction. When the acidified solution is treated with potassium bismuth iodide it gives a brick-red precipitate. It gives the murexide reaction. With sulphuric and hydrochloric acids it gives readily soluble salts. The chloroplatinate, and especially the picrate, are difficultly soluble in water. The gold double salt is also not very soluble. Kossel and Steudel give no melting- or decomposing-point for their cytosine, but state that the picrate turned brown on heating to 255° and melted at 270° with decomposition.

2-Oxy-6-aminopyrimidine Picrate.—Picric acid produced an immediate precipitate, which crystallized in bright-yellow needles or very slender, needle-like prisms. When made from material that had not been decolorized with animal charcoal, and therefore containing a slight impurity, it decomposed with violent effervescence quite sharply at about 264°. When prepared from the pure oxyaminopyrimidine the crystals had a more pronounced prismatic habit and they showed no melting-point, but sintered, became black, and decomposed at about 300° to 305°. One hundred parts of water dissolve 0.076 parts of the salt at 25°. Our experience with these picrates has shown that the melting-points are rather indefinite. They can be made to effervesce at a somewhat higher or lower temperature, according to the rate of heating. They are difficult to analyze on account of the ease with which oxides of nitrogen pass over. A nitrogen determination of a sample prepared from the pure base, for example, gave :

	Calculated for $C_4H_5ON_3.C_6H_2(NO_2)_3OH$.	Found.
N	24.7	26.4

The *chloroplatinate* separates as a precipitate in yellow flakes. A platinum determination gave :

	Calculated for $(C_4H_5ON_3)_2H_2PtCl_6$.	Found.
Pt	30.83	30.60

2-Oxy-6-acetaminopyrimidine was prepared by heating 0.5 gram of the amino derivative with acetic anhydride. It proved to be practically insoluble in alcohol and difficultly soluble in water. It crystallized from hot water in colorless, microscopic prisms, with rough faces, frequently occurring in crosses. It showed no signs of melting at 300°. A nitrogen determination gave :

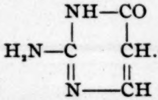
	Calculated for $C_6H_7O_2N_3$.	Found.
N	27.44	27.82

The *phenyl isocyanate derivative* was prepared by heating 0.5 gram of the base with 0.55 gram of phenylisocyanate on the steam-bath for six hours. The white crystalline product which resulted proved to be very insoluble. It was boiled repeatedly with alcohol and then digested with water. The insoluble material thus obtained began to sinter on heating at about 255°, and then melted with violent effervescence at 260°. A nitrogen determination agreed with the calculated for an addition of 2 molecules of phenyl isocyanate to one of the base.

	Calculated for		
	(1 : 1) $C_{11}H_{10}O_2N_4$.	(2 : 1) $C_{18}H_{15}O_3N_5$.	Found.
N	24.34	20.05	20.4

Action of Bromine.—Three-tenths gram of 2-oxy-6-aminopyrimidine was treated with 1 gram of glacial acetic acid, and 0.5 gram of bromine was added. An immediate reaction took place, heat was evolved, and an orange powder separated, which dissolved on warming. Some water was added to the cooled solution and the precipitate produced was crystallized from water. It formed well-crystallized, colorless needles, and it melted sharply at 247° with effervescence. When dissolved in water and made alkaline with ammonia it gave a strong, wine-red color, and, on cooling, a brick-red substance separated. This had no definite melting-point.

2-Amino-6-oxypyrimidine,



$$\begin{array}{lcccl} & \mathrm{NH} & - & \mathrm{CO} \\ & | & & | \\ \mathrm{H_2N}- & \mathrm{C} & & \mathrm{CH}. \\ & \| & & \| \\ & \mathrm{N} & - & \mathrm{CH} \end{array}$$

—Thirty grams of guanidine carbonate were dissolved in 100 cc. of water and mixed with 54 grams of crystallized barium hydrate in 400 cc. of water. The solution was filtered and 55 grams of sodium ethyl formylacetate were added. The whole dissolved except a slight sediment. After standing for three hours the solution was divided into two equal portions. One was allowed to stand over night, the other was warmed on the steam-bath for a few minutes, and then just acidified with sulphuric acid. The filtered solution on evaporation, and adding ammonia in excess, gave a crystalline, brown precipitate, weighing 6.7 grams, or 36 per cent of the calculated. The portion that stood over night, on similar treatment, gave practically the same yield, so that long standing does not better the yield. In another experiment 10 grams of guanidine carbonate and 22 grams of sodium ethyl formylacetate gave 4.8 grams of the base, which is a yield of 39 per cent of the calculated. On boiling the crude products with animal charcoal, in aqueous solution, the color is slowly removed and, on cooling, small, flat, colorless, transparent prisms generally separate. These crystals, when air-dried, contained less than 0.5 per cent of water. A nitrogen determination (I.) gave:

I. 0.0900 gram substance gave 30.6 cc. of moist N at 26°.5 and 762 mm. pressure.

II. 0.1357 gram substance gave 44.8 cc. of moist N at 24° and 768 mm. pressure.

	Calculated for $C_4H_5ON_3$.	Found. I.	II.
N	37.83	37.98	37.45

In another experiment, as above, the base was crystallized from water, purified with animal charcoal, and when a portion had separated from the still warm solution, in the form of prisms, the mother-liquor was decanted. It then became almost semi-solid from the separation of a mass of long, slender, colorless, silky needles which, on drying in the air, formed a bulky, felt-like mass. This material contained, or occluded, water, but the determinations were not constant: 0.8567 gram substance lost 0.1036 gram on heating to 100° to 110°, equivalent to 12.0 per cent water. The needle form appears to result also from dilute solutions or on rapidly cooling. 2.0527 grams of substance prepared in this manner, on standing in the air for eight or nine hours and then heating, lost 0.1657 gram, equal to 8.7 per cent of water. The calculated for 1 molecule of water is 13.9 per cent. A nitrogen determination of the dried material is given above (Analysis II.).

Properties of 2-Amino-6-oxypyrimidine.—It was found that the needles gave the stout prisms and the prisms could be obtained in needle form under slight changes in the crystallization. The crystals were not suitable for crystallographic measurements, the faces being highly etched, especially the end faces of the prisms. The material melts, or rather decomposes, with violent effervescence, at about 276°. This effervescing-point may vary several degrees, according to the rate of heating.

The base is precipitated by phosphotungstic acid. It is not precipitated by potassium bismuth iodide in hydrochloric acid solution, but it gives a brick-red precipitate in solutions of the base in sulphuric acid. It gives the murexide reaction. Its sulphate and hydrochloride are readily soluble in water and the former crystallizes in flat prisms. The picrate is very difficultly soluble and the gold and platinum double salts are also not very soluble. When heated with 20 per cent sulphuric acid for two hours, at 145° to 150°, a portion of the material is converted into uracil.

2-Amino-6-oxypyrimidine Picrate.—When picric acid is added to a hot solution of the base in water a mass of bright-yellow needles separate. If slowly cooled slender prisms are formed. On heating, the crystals become less transparent at about 180°, showing evidence of darkening at about 255°, and signs of melting at 270°. Between this point and 280° they generally effervesce. They dissolve in about 1200 to 1300 parts of water at 25°. A nitrogen determination gave :

	Calculated for $C_4H_5ON_3.C_6H_2(NO_2)_3OH$.	Found.
N	24.70	24.72

The *chloroplatinate* separates in the form of small yellow needles, which form acicular crystals or spikes on slowly cooling the hot solutions. On heating, it decomposes above 200°, becoming brown, but not melting below 286°. A platinum determination gave :

	Calculated for $(C_4H_5ON_3)_2H_2PtCl_6$.	Found.
Pt(=194.8)	30.83	30.56

The *gold chloride double salt*, which seems to be more soluble than the platinum double salt, forms bright-yellow, stout prisms, which easily form a supersaturated solution. A gold determination gave :

	Calculated for $C_4H_5ON_3.HCl.AuCl_3$.	Found.
Au(=195.7)	43.51	43.57

2-Acetamino-6-oxypyrimidine.—One-half gram of the base required about 7.5 grams of boiling acetic anhydride to effect solution. On cooling, a colorless mass of crystals separated, so bulky that the test-tube could be inverted without loss of the contents. This material crystallizes in bunches of minute mother-of-pearl scales from alcohol, and it melts at 247° to a clear liquid. A nitrogen determination gave:

	Calculated for $C_6H_7O_2N_3$.	Found.
N	27.45	27.69

2-Amino-5-brom-6-oxypyrimidine.—Three grams of the base were suspended in 20 cc. of glacial acetic acid, in which it is difficultly soluble, and 4.5 grams of bromine were dropped in. The action took place smoothly and an orange powder separated. It weighed 6.6 grams, while the calculated amount for a hydrobromide of 2-amino-5-brom-6-oxypyrimidine is 7.2 grams. The yield obtained was 83 per cent of the theoretical. This hydrobromic acid salt forms long, slender, needle-like prisms, when crystallized from water, and it melts at about 273° with strong effervescence. When the aqueous solution of this is treated with ammonia the brom-base separates as a compact, granular precipitate, insoluble in alcohol and extremely difficultly soluble in water. It crystallizes from strong acetic acid in radiating masses of pointed plates, and it melts with decomposition at about the same temperature as the hydrobromide or the bromine-free base. It has acid properties and it dissolves in strong ammonia, but separates again unaltered on boiling off the ammonia. A nitrogen determination gave:

	Calculated for $C_4H_4ON_3Br$.	Found.
N	22.10	22.13

NEW HAVEN, CONN., March 20, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CIV.—ON CYTOSINE OR 2-OXY-6-AMINOPYRIMIDINE FROM TRITICO-NUCLEIC ACID.

By Henry L. Wheeler and Treat B. Johnson.

It has been shown by Osborne and Harris[1] that uracil can be obtained from the nucleic acid of the wheat embryo.[2] As we wished to compare our synthetic uracil with some of the natural we asked Dr. Osborne for a sample. Not having the pure substance at hand, he very kindly supplied us with 1.35 grams of material obtained by evaporating the mother-liquors from the crystallization of his uracil.

We found that the material, after crystallizing six times from water, gave a solution which, on slowly evaporating, deposited flat, needle-like crystals, about a centimeter in length. This material was obviously not uracil, and, at Dr. Osborne's suggestion, we then examined the material for cytosine. We found, in fact, that it consisted of a mixture of apparently about equal parts of uracil and cytosine.

When a solution of 3 grams of picric acid, dissolved in 200 cc. of hot water, was added to the 1.35 grams of material dissolved in 50 cc. of hot water and the mixture was allowed to stand for twelve hours, beautiful, long, silky, bright-yellow needles separated. The weight of the picrate obtained was 1.7 grams. The needles, which had every appearance of purity, melted with effervescence, as Kossel and Steudel[3] state in the case of thymus cytosine at about 270°, turning brown a number of degrees below this temperature.[4] We took exactly 1 gram of this picrate for the preparation of the free base. The picrate was treated with an excess of sulphuric acid and the picric acid was removed by shaking with ether. The sulphuric acid was mostly removed by barium hydrate, and, on concentrating and adding ammonia, colorless, well-crystallized, slender, needle-like prisms of the free base separated. The amount of this material was 0.1641 gram. This, after washing with water, was dried by standing in the air, on paper, for twelve hours. It then lost 0.0181 gram on heating to constant weight at 110° to 120°, equivalent to 11.30 per cent of water, while the calculated for $C_4H_5ON_3.H_2O$ is 13.9 per cent water.

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[1] Ztschr. physiol. Chem., **36**, 85; Annual Report for 1901 of the Connecticut Agricultural Experiment Station, page 408.

[2] Osborne and Campbell: J. Am. Chem. Soc., **22**, 379.

[3] Ztschr. physiol. Chem., **37**, 378 (1903).

[4] Owing to the ease with which this picrate gives off oxides of nitrogen, the analytical results came high both for carbon and nitrogen, so that the results were without value. In this connection it may be stated that a nitrogen determination gave 26.5 per cent nitrogen, while a precisely similar result was obtained in the case of the picrate from the synthetic base, namely 26.4 per cent nitrogen. The calculated for $C_4H_5ON_3.C_6H_2(NO_2)_3OH$ is 24.7 per cent nitrogen.

This base melted with strong effervescence at about 323°, precisely like the synthetical 2-oxy-6-aminopyrimidine, and when a portion was mixed with the latter substance the melting- or effervescing-point was not lowered.

After determining the solubility in water (see below) the base was then converted into the chloroplatinate. A platinum determination gave:

0.0830 gram substance gave 0.0253 gram platinum.

	Calculated for $(C_4H_5ON_3)_2H_2PtCl_6$.	Found.
Pt(=194.8)	30.83	30.48

The remaining material was given to Professor S. L. Penfield for a crystallographic examination and comparison with the corresponding platinum double salt prepared from 2-oxy-6-aminopyrimidine. Kossel and Steudel[1] state, in regard to the platinum chloride double salts prepared by them, that "Das Platindoppelsalz des Störcytosins zeigte nämlich fast durchweg doppelbrechende Zwillingsformen, welche in der Weise aneinander gelagert waren, dass die Auslöschungsrichtung in dem einen Krystall einen Winkel von 53° mit der Auslöschungsrichtung des anderen Krystalls bildete. Diese Winkel wurden beim Cytosin aus Herings-und Störtestikeln gleich befunden, beim Cytosin aus Thymusnucleinsäure haben wir bisher solche Zwillingsformen überhaupt nicht beobachtet."

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[1] Ztschr. physiol. Chem., **37**, 379 (1903).

Crystallography of 2-Oxy-6-aminopyrimidine Chloroplatinate (Synthetic Cytosine Chloroplatinate).

The crystals submitted for study were thin plates and for examination with the microscope they were embedded in oil, and over them a cover glass was placed.

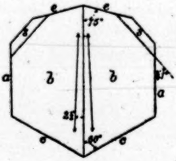


Fig. I.

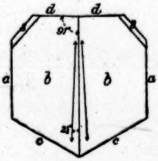


Fig. II.

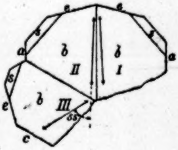


Fig. III.

Figure I. represents the habit of one of the crystals which was unbroken and of almost ideal symmetry. It is a twin, presumably belonging to the monoclinic system, the large flat face *b* being the clinopinacoid (010). The edges *c*, *a*, and *e* appear as sharp lines under the microscope, and represent the direction of faces at right angles to *b*. It may be assumed that *c* is the base (001) and *a* the orthopinacoid (100), the inclination of the axes, β, being about 60°. Some beveling form, *s*, appears at the upper corners, which may be taken as the monoclinic pyramid $(\bar{1}11)$, its intersection with *b* making an angle of about 41° with the vertical axis (the trace of *a*), as indicated in the figure. The faces *e* at the top are orthodomes, inclined about 75° to the vertical axis, and they have the symbol $(\bar{1}02)$. The twinning plane, uniting the two individuals, is the orthopinacoid *a*. The extinction, indicated in the figure by the arrows, is inclined about 2°.5 either side of the twinning plane.

A second crystal, Fig. II., was like the one just described, except for the faces *d* at the top, which make an angle of about 91° with the vertical axis. The form *d* is evidently an orthodome, and has the symbol $(\bar{1}03)$.

A third crystal, Fig. III., showed two kinds of twinning. Crystals I. and II. are twinned about the orthopinacoid as in

Fig. I., while II. and III. have the base *c* as the twinning plane. The extinction is indicated by the arrows. In crystals II. and III. the extinction directions make an angle of 55° with one another.

Crystallography of Wheat Cytosine Chloroplatinate.

The crystals submitted for study were much thinner than those prepared from synthetic cytosine, hence when mounted in oil for examination they were much more broken.

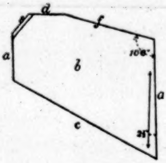


Fig. IV.

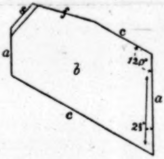


Fig. V.

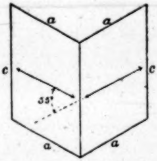


Fig. VI.

Fig. IV. represents a fragment of a twin crystal, the part to the right of the twinning plane not being shown. The arrangement of the faces and the angles is like Fig. II., except *f*, at the top, which makes an angle of 106° with the vertical axis and corresponds to an orthodome $(\bar{1}06)$.

Fig. V. represents a part of another twin crystal, like Fig. IV., except that *f* and *c* terminate the crystal instead of *d* and *f*. The extinction was 2°.5 from the vertical axis as in the case of the synthetic preparation.

Among the broken fragments two kinds of twinning were observed, some with *a* as the twinning plane and others like Fig. VI., with the base *c* as the twinning plane. In the latter the twinning law is the same as that of crystals II. and III. of Fig. III. The extinction is nearly parallel to *a*, and makes an angle with the twinning plane of 62°.5, or the two extinction directions make an angle of 55° with one another.

Aside from the extinction directions the optical properties of the crystals were not very decisive. When examined in convergent light an indistinct interference figure was seen, presumably the center of the cross of an obtuse bisectrix.

The identity of the synthetic cytosine and wheat cytosine is established beyond question by the crystallographic similarity of the two chloroplatinates.

The measurements given were made under the microscope, and only approximate accuracy is claimed for them. The symbols of the domes *e* ($\bar{1}02$), *d* ($\bar{1}03$), and *f* ($\bar{1}06$) were determined by plotting.

Dr. P. A. Levene has very kindly sent us a pure sample of his base from the spleen which has the properties and composition of Kossel and Steudel's cytosine. The amount of this at our disposal was about 0.12 gram. It formed thin, flat, colorless crystals or prismatic plates, and it melted or effervesced, side by side with the synthetic material at 323°, and, when portions of these substances were mixed, the melting-point was not altered in the slightest. After determining the solubility we converted this material into the chloroplatinate. Professor Penfield then reported on the crystallography as follows:

Crystallography of Spleen Cytosine Chloroplatinate.

The crystals are like the ones previously described, having the same angles, though presenting some variation in habit. Fig. VII. is typical, showing *a*, *b*, *c*, and *s* forms, but with

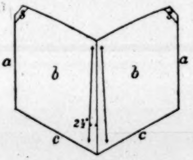


Fig. VII.

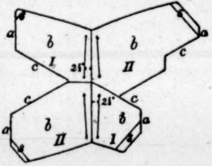


Fig. VIII.

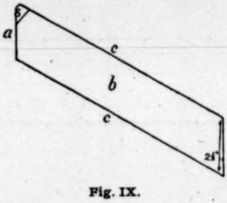


Fig. IX.

the reentrant angle at the top having a curved contour so that no definite symbol can be assigned. The extinction, as in the other preparations, is 2°.5 either side of the twinning plane, as indicated by the arrows in the figure.

Fig. VIII. represents a penetration twin, drawn with camera lucida. The two opposite parts I. and I. extinguish simultaneously, as also II. and II. Many crystals of the crop submitted for examination were long, lath-shaped individuals, Fig. IX. Several having this habit were twinned about the *c* face.

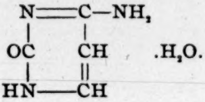
The three chloroplatinates prepared from synthetic cytosine, wheat cytosine, and spleen cytosine are crystallographically identical and show no greater variation in habit than is generally observed on crystals of any substance formed under varying conditions.

The solubility of the three samples of cytosine in water at 25° was determined with the following results:

100 parts water dissolve 0.83 part wheat cytosine.
100 parts water dissolve 0.78 part spleen cytosine.
100 parts water dissolve 0.79 part synthetic cytosine.

The high result in the case of wheat cytosine is probably due to the fact that it was not as pure as the others. Owing to lack of material the determination was made with the above-mentioned sample, which had been washed but not recrystallized from water.

We conclude, from these results, that the products obtained from the three different sources are identical, and that cytosine, is as Kossel and Steudel have predicted, an oxyaminopyrimidine, *viz.*, 2-oxy-6-aminopyrimidine. Its structure is to be represented by the following formula, or a tautomeric form:



Hitherto cytosine has been found only in animal organs. The present results offer further evidence of the similarity of nucleic acids of animal and vegetable origin.

We take pleasure in thanking Dr. Osborne and Dr. Levene for the material placed at our disposal and Professor Penfield for the crystallographic descriptions.

NEW HAVEN, CONN., March 25, 1903.

IDENTIFICATION OF ORGANIC ACIDS BY THEIR TOLUIDES.

BY HEYWARD SCUDDER.

It is customary to make anilides and toluides by heating the base with the anhydride or chloride of the acid. When only a small amount of the acid is available it may be necessary to prepare as little as 0.1 gram of the anhydride or chloride, a troublesome matter if the derivative is liquid, unless one is in the habit of handling small quantities.

The following modification of Petersen's[1] method of preparing amides from the sodium salt of the acid does away with the need of preparing an anhydride or chloride. The sodium salt need not be anhydrous, so that the time necessary for drying is not lost, and the reaction itself is moderately rapid. The time factor is of some importance in making derivatives for the purpose of identification, since under these conditions rapidity is more essential than getting a large yield, provided always that the yield obtained from a small amount of the acid is sufficient to be purified easily. *p*-Toluidine is chosen as the base because the *p*-toluides of most acids are solid, and there is usually a greater difference between the melting-points of the *p*-toluides of two adjacent acids in a series, *e. g.*, acetic and propionic, than between those of the isomeric toluides or of the anilides of the same acids.

Procedure.—Mix in a dry 6-inch test-tube 1 to 1.2 grams of *p*-toluidine and 0.3 to 0.4 cc. concentrated hydrochloric acid (sp. gr. 1.2). Add about 0.4 gram of the sodium salt of the acid. Support the test-tube in a clamp, resting the bottom of the tube in a hole 1 centimeter in diameter cut through a piece of asbestos felt. The asbestos prevents overheating the sides of the tube. Heat for one hour over a small flame. The height of the flame should be so regulated that the toluidine vapor condenses on the sides of the tube between one-third and one-half way from the bottom. If the sodium salt is anhydrous, the ring formed on the sides of the tube by the condensing toluidine will be distinct. But if the salt contains water of crystallization the water will condense all the way up to the top of the tube and the ring may not be clearly marked. In such a case it is advisable to remove the flame for a minute or two after heating for twenty minutes. When the heating is resumed the ring will be visible.

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[1] Ann. Chem. (Liebig), **107**, 331 (1858).

The toluide is best purified by crystallization from benzene or petroleum ether, in which a resin-like body that forms is very soluble. This resin can also be removed by boiling with water (which dissolves the toluide) and filtering hot, leaving the resin on the filter. In such a case it is usually best to boil the filter and resin in a few cubic centimeters of water and filter hot into the first filtrate, for the resin holds the toluide tenaciously, and keeps back a surprising amount, unless care is taken that the boiling is sufficiently prolonged to leave only a very thin layer of resin on the filter. The resin is readily soluble in alcohol. If the toluide is not white, a second crystallization is necessary.

The yield is good. In the case of acetic acid 0.4 gram of the sodium salt containing water of crystallization corresponds to about 0.2 gram of the acid. If one has had experience in handling small quantities it is possible to get sufficient of the toluide from 0.1 gram of the sodium salt. If less of the sodium salt is used than is called for in the preceding directions, the quantity of hydrochloric acid should be diminished correspondingly. But the quantity of *p*-toluidine should never be less than 0.5 gram, otherwise so little is left in the bottom of the tube when the mixture begins to boil that overheating occurs, and the proper reaction does not take place. An excess of hydrochloric acid must not be used.

This reaction has been tried on a number of acids and found to be generally available. Formic acid gives chiefly oxaltoluide instead of formtoluide.

If a volatile acid (as one of the lower fatty acids) is present in solution, the proper weight of the salt can be obtained by distilling the acid into a solution of 0.12 to 0.14 gram of sodium hydroxide in 3 cc. of water colored by phenolphthaleïn, until the color has disappeared, and then boiling the solution down to dryness. The presence of moderate amounts of sodium chloride or sulphate do not influence the reaction.

In the case of most solid acids and acids of high boiling-point, it is not necessary to use the sodium salt, but 0.1 gram of the acid itself can be heated with the *p*-toluidine and hydrochloric acid as directed. The presence of the hydrochloric acid has a great effect on the rapidity of the reaction in some cases. Thus 0.1 gram of benzoic acid heated for one hour with 0.7 gram *p*-toluidine gave a very small yield of toluide. The same amounts of benzoic acid and toluidine, to which 0.1 cc. of concentrated hydrochloric acid had been added, gave a good yield when heated for only one-half hour. Oxalic acid and most acids that readily form anhydrides by the action of heat alone do not need the addition of hydrochloric acid.

The time required to get a sufficient yield of toluide varies greatly. One hour's heating has been found sufficient. But it is longer than is necessary in many cases. Oxalic acid gives an excellent yield when heated for only ten minutes. The experiments made with sodium oxalate were carried out with one hour's heating, but there is no reason to believe that this shorter period would not have been sufficient, for the organic acid is, of course, liberated when the mixture is heated.

Other salts, as barium, calcium, ammonium, etc., work quite as well as the sodium salts. Some toluides, *e.g.*, propiontoluide, are quite volatile at temperatures considerably below their melting-points, and cannot safely be dried at 100°.

Detailed directions for the best methods of rapid preparation of the anilides and toluides of a number of organic acids, as a means of identification, will soon be published by Dr. S. P. Mulliken, of this laboratory, in his "Method of Qualitative Organic Analysis."

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, February, 1903.

REVIEWS.

EXERCISES IN QUALITATIVE CHEMISTRY, CHIEFLY INORGANIC. By JOHN WHITE, PH.D., Professor of General and Analytical Chemistry, University of Nebraska. New York: Henry Holt & Co. 1901.

Professor White's manual is intended (to quote the author's preface) "to enable the student to complete for himself by purely inductive methods a fairly complete conception of analytical processes." For example, the student studies the reactions on barium, calcium, and strontium salts, respectively, of alkali oxalate, carbonate, dichromate, and phosphate. He is then asked to devise and test a method for detecting and separating these metals. The book is not intended to supplant the instructor. Indeed, its usefulness would depend on the criticism and explanations of the teacher. Professor White's book is simple, clear, and suggestive.

E. R.

A BRIEF COURSE IN QUALITATIVE CHEMICAL ANALYSIS FOR SCHOOLS AND COLLEGES. By JOHN B. GARVIN, B.S. (University of Illinois), Instructor in Chemistry in East Denver High School, Denver, Colorado. Boston: D. C. Heath & Co. 1902.

Mr. Garvin's manual is in the first part similar to that of Professor White, but while the latter is written for college students, Mr. Garvin's book is briefer and better adapted to the use of schools. The book consists of three parts: a study of bases, a study of acids, and a scheme for systematic qualitative analysis. It is well and carefully written. E. R.

CHEMISTRY BY OBSERVATION, EXPERIMENT, AND INDUCTION. A Laboratory Manual for Students. By J. I. D. HINDS, PH.D., Professor of Chemistry in the University of Nashville. New York: John Wiley & Sons. 1902.

This is a simple laboratory manual to be used with the author's "Inorganic Chemistry." E. R.

TEXT-BOOK OF ELECTROCHEMISTRY. By SVANTE ARRHENIUS, Professor at the University of Stockholm. Translated by JOHN MCCRAE, PH.D. London, New York, and Bombay: Longmans, Green & Co. 1902.

The English edition of the Electrochemistry by this celebrated man has recently appeared. The author states that the basis of the book is a series of lectures delivered at the University of Stockholm. The character of the work can be seen best from the contents. The subject is treated in seventeen chapters, having the following titles: Fundamental physical and chemical conceptions, older electrochemical views, the laws of Avogadro and van 't Hoff, vapor-pressure of solutions, boiling-point and freezing-point of solutions, general conditions of equilibrium, velocity of reactions, electrolytes, electrolytic dissociation, conductivity of electrolytes, degree of dissociation and dissociation constant, conclusions from the dissociation theory, additive properties of solutions, equilibrium between several electrolytes, calculation of electromotive forces, potential difference between two bodies, oxidation and reduction elements, secondary elements, electro-analysis, development of heat by the electric current.

The English translation is from the German translation of the original, which was in Swedish. The appearance of two translations so quickly after the original was published would indicate a large demand for the work. H. C. J.

JAHRBUCH DER ELEKTROCHEMIE. Begründet und bis 1901 herausgegeben von W. NERNST, o. Professor an der Universität Göttingen, und W. BORCHERS, o. Professor an der Technischen Hochschule zu Aachen. Berichte über die Fortschritte des Jahres 1901. Herausgegeben von DR. HEINRICH DANNEEL, Privatdocent der physikalischen Chemie und der Elektrochemie an der Technischen Hochschule zu Aachen. VIII. Jahrgang. Verlag von Wilhelm Knapp, Halle a. S. 1902.

As will be seen from the above, the editorship of the Jahrbuch der Elektrochemie has been transferred from Nernst and Borchers to Danneel. He is, however, assisted by a number of co-workers, as Kenasy, Elbs, Harms, Kügelgen, and Mugdan.

The work appears, as formerly, under the two heads: Scientific Part and Applied Electrochemistry. The scientific part begins with a discussion of such general matters as laboratories, books on electrochemistry, general electrical apparatus, and new methods of work. The new contributions to the general theories of electrochemistry are then reviewed, and this is followed by reviews on conductivity of solutions, electrical energy, polarization, and electrolysis.

The applied electrochemistry begins with a review of the recent work on primary and secondary cells. This is followed by a review of the recent work on inorganic products produced by means of the electric current, including both metallic and metalloid elements, their carbides, and much more complex compounds such as sulphuric acid, perchlorides, etc.

The applications of electricity to organic chemistry, made in 1901, are then reviewed. These include the electrosynthesis of organic compounds, and the electrolytic reduction and oxidation of organic substances.

The reviews, on the whole, appear to be clear, comprehensive, and concise, and one can find here in a comparatively short compass what would require very wide reading to obtain directly from the original articles. The work is undoubtedly well worth doing, and will contribute largely to the understanding and development of electrochemistry both pure and applied. H. C. J.

KURZE ANLEITUNG ZUR MAASSANALYSE MIT SPEZIELLER BERÜCKSICHTIGUNG DER VORSCHRIFTEN DES ARZNEIBUCHES. VON DR. LUDWIG MEDICUS. Siebente und achte, verbesserte und vermehrte Auflage. 1902. Tübingen: Verlag der H. Laupp'schen Buchhandlung.

The book deals with the elementary principles of volumetric analysis with special reference to the application of these principles to testing pharmaceutical products. General methods are given for the various processes involved in alkalimetric, acidimetric, iodometric, oxidation, and precipitation analyses. Under each chapter details are given for the testing of the various pharmaceutical products. No attempt is made to discuss any of the processes critically, and the worker is led to believe that each method will proceed as smoothly as it is represented on paper. It is questionable whether a book of this nature is at all useful to any other than the particular class for whom it is intended. The pharmacist would, however, be able to get from it a very clear statement of the facts in regard to volumetric analysis, and would in most cases be able to make satisfactory analyses of the products offered him.

In an appendix are given methods for the determination of carbon dioxide in air, the analysis of water, and the determination of the more important constituents of wine. That the book has been found useful is indicated by the number of editions through which it has passed. H. F.

PLATTNER'S MANUAL OF QUALITATIVE AND QUANTITATIVE ANALYSIS WITH THE BLOWPIPE. Translated from the sixth German edition by HENRY B. CORNWALL, A.M., PH.D., with the assistance of JOHN H. CASWELL, A.M. New York: D. Van Nostrand Company. 1902. pp. xvii + 463. Price, $4.50.

This book has long been recognized as one of the few standard works on analytical chemistry, and as such it is more or less familiar to every student of chemistry. This new and revised edition is thoroughly up-to-date. Many new minerals have been introduced, while tests and determinations of little value have been discarded. Spectroscopic methods have been omitted and modern chemical notation has been introduced. The book in its present form will be welcomed by the mineralogist, the chemist, and all who have to do with blowpipe analysis. F. H. G.